

Mn(III)-induced reaction of 1,1-diarylethenes with potassium thiocyanate: a novel synthesis of dithiocyanates

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Abstract

Reactions of 1,1-diarylethenes with potassium thiocyanate in the presence of manganese triacetate dihydrate was uncovered to be a simple approach to dithiocyanates. This new method was applied to synthesize some new 1,2-dithiocyanatoethane derivatives. High yields and unbelievable short reaction time as well as simple procedure made this synthetic method become a practical alternative to reported ones.

Keywords. Mn(III)-oxidative reaction, 1,1-diarylethenes, dithiocyanates.

1. INTRODUCTION

Thiocyanates and dithiocyanates are such a versatile class of sulfur-containing organic compounds that their synthesis has been receiving considerable attention. The most basic synthetic method for thiocyanates is the nucleophilic substitution reactions in aqueous media. Triphenylphosphine/diethylazodicarboxylate (DEAD)/NH₄SCN, for instance, were successfully used for the conversion of alcohols, thiols, carboxylic acids, silyl ethers, and silyl carboxylates to their corresponding thiocyanates [1]. Ionic liquid [bmim][SCN] was also reported to be an efficient reagent for nucleophilic substitution reactions of sulfonate esters derived from primary and secondary alcohols [2]. The nucleophilic substitution reactions may be assisted by microwave [3] or supporting polymer [4]. Very recently, several methods for thiocyanation of heterocyclic compounds have also been described [5]. On the other hand, established methods for the synthesis of dithiocyanates are really rare. Cerium(IV) ammonium nitrate (CAN)/NH₄SCN were used to prepare dithiocyanates from aralkenes [6] while [bis(acetoxy)iodo]benzene/trimethylsilyl isothiocyanate were employed for the dithiocyanation of alkenes [7]. Dithiocyanation by radical additions was performed by using iodobenzenediacetate (IBDA)/KSCN/Mg(ClO₄)₂ and IBDA/KSCN/TEMPO reagent combinations [8] or ferric(III) chloride [9]. Speaking of radical addition, we have had a longstanding interest in the synthesis of heterocycles using free radicals generated by the

Mn(III)-oxidative system [10]. We speculated that manganese(III) oxidant could be used to produce radical from thiocyanate anion and thus, provided a practical route to dithiocyanate derivatives. With this in mind, we carried out reactions of 1,1-diarylethenes with potassium thiocyanate in the presence of manganese triacetate dihydrate. In this paper, results of our work will be presented.

2. EXPERIMENTAL

2.1. Measurements

All of the ¹H and ¹³C NMR spectra were recorded on a JNM-AL 300 FT NMR spectrometer at 300 MHz for ¹H and 75 MHz for ¹³C or on a Bruker Avance 500 FT NMR spectrometer at 500 MHz for ¹H and 125 MHz for ¹³C, with tetramethylsilane as the internal standard. The chemical shifts are shown in δ values (ppm) and coupling constants in Hz. The IR spectra were measured on a Thermo Scientific Nicolet iS5 FT-IR spectrometer and the IR spectral data are expressed in cm⁻¹.

2.2. Materials

Manganese(III) acetate dihydrate, Mn(OAc)₃·2H₂O, was prepared according to the literature method [11]. 1,1-Diarylethenes **1a-d** were prepared by dehydration of the corresponding alcohols, which were synthesized from substituted acetophenones and arylmagnesium bromides [12] and their NMR data are given below. Manganese(II)

acetate tetrahydrate was purchased from Wako Pure Chemical Ind., Ltd., potassium thiocyanate and glacial acetic acid from Sigma-Aldrich Corp. and all were used as received.

1,1-Diphenylethene (1a): ^1H NMR (CDCl_3 , δ , ppm) 7.31-7.27 (10H, m, arom H), 5.44 (2H, s, $=\text{CH}_2$); ^{13}C NMR (CDCl_3 , δ , ppm) 150.00 ($>\text{C}=\text{}$), 141.44 (2C) (arom C), 128.23 (4C), 128.12 (4C), 127.67 (2C) (arom CH), 114.27 ($=\text{CH}_2$).

1,1-Bis(4-methylphenyl)ethene (1b): ^1H NMR (CDCl_3 , δ , ppm) 7.23 (4H, d, $J = 8.1$, arom H), 7.12 (4H, d, $J = 8.1$, arom H), 5.38 (2H, s, $=\text{CH}_2$), 2.36 (6H, s, Me x 2); ^{13}C NMR (CDCl_3 , δ , ppm) 149.72 ($>\text{C}=\text{}$), 138.78 (2C), 137.40 (2C) (arom C), 128.79 (4C), 128.16 (4C) (arom CH), 112.97 ($=\text{CH}_2$), 21.15 (Me x 2).

1,1-Bis(4-chlorophenyl)ethene (1c): ^1H NMR (CDCl_3 , δ , ppm) 7.29 (4H, d, $J = 8.4$, arom H), 7.22 (4H, d, $J = 8.4$, arom H), 5.43 (2H, s, $=\text{CH}_2$); ^{13}C NMR (CDCl_3 , δ , ppm) 147.87 ($>\text{C}=\text{}$), 139.42 (2C), 133.83 (2C) (arom C), 129.45 (4C), 128.44 (4C) (arom CH), 115.08 ($=\text{CH}_2$).

1,1-Bis(4-methoxyphenyl)ethene (1d): ^1H NMR (CDCl_3 , δ , ppm) 7.28 (4H, d, $J = 8.7$, arom H), 6.84 (4H, d, $J = 8.7$, arom H), 5.28 (2H, s, $=\text{CH}_2$), 3.80 (6H, s, $(-\text{OMe} \times 2)$); ^{13}C NMR (CDCl_3 , δ , ppm) 159.24 (2C) (arom C), 148.90 ($>\text{C}=\text{}$), 134.22 (2C) (arom C), 129.38 (4C), 113.42 (4C) (arom CH), 111.63 ($=\text{CH}_2$), 55.20 ($-\text{OMe} \times 2$).

2.3. Reaction procedure

A general procedure is as follows: 1,1-Diarylethene (0.5 mmol) was weighed into a 30 mL flask equipped with a magnetic stirrer. Potassium thiocyanate (1-2 mmol) and glacial acetic acid (10 mL) were added. The flask was placed in an appropriate temperature oil bath and the mixture was stirred. Manganese (III) acetate dihydrate (0.5-1 mmol) was added and the reaction was allowed to proceed until the reaction mixture turned into colorless or yellow. The solvent was removed *in vacuo*, and the residue was quenched with water. The aqueous mixture was extracted three times with chloroform. The combined extract was concentrated to dryness. The products were separated on silica gel TLC (Merck Kieselgel 60 F₂₅₄) with chloroform as the developing solvent.

2.4. Product data

1,1-Diphenyl-1,2-dithiocyanatoethane (3a): colorless liquid; IR (cm^{-1}) 2158.43 ($-\text{SCN}$); ^1H NMR (CDCl_3 , δ , ppm) 7.45-7.23 (10H, m, arom H),

3.99 (2H, s, $-\text{CH}_2-$); ^{13}C NMR (CDCl_3 , δ , ppm) 140.00 (2C) (arom C), 129.11 (4C), 128.74 (2C), 126.10 (4C) (arom CH), 111.16, 111.13 ($-\text{SCN}$), 72.08

($>\text{C}=\text{}$), 46.53 ($-\text{CH}_2-$).

1,1-Bis(4-methylphenyl)-1,2-dithiocyanatoethane (3b): colorless liquid; IR (cm^{-1}) 2160.26 ($-\text{SCN}$); ^1H NMR (CDCl_3 , δ , ppm) 7.40-7.19 (8H, m, arom H), 3.97 (2H, s, $-\text{CH}_2-$), 2.40 (6H, s, Me x 2); ^{13}C NMR (CDCl_3 , δ , ppm) 139.00 (2C), 137.29 (2C) (arom C), 129.75 (4C), 126.02 (4C) (arom CH), 111.40, 109.58 ($-\text{SCN}$), 71.90 ($>\text{C}=\text{}$), 46.70 ($-\text{CH}_2-$), 21.07 (Me x 2).

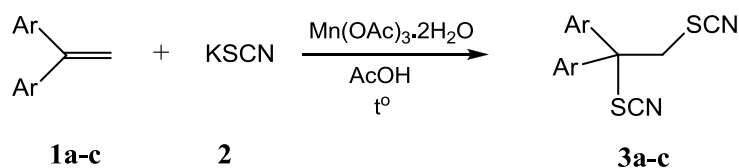
1,1-Bis(4-chlorophenyl)-1,2-dithiocyanatoethane (3c): colorless liquid; IR (cm^{-1}) 2160.26 ($-\text{SCN}$); ^1H NMR (CDCl_3 , δ , ppm) 7.40 (4H, d, $J = 8.5$, arom H), 7.24 (4H, d, $J = 8.5$, arom H), 3.95 (2H, s, $-\text{CH}_2-$); ^{13}C NMR (CDCl_3 , δ , ppm) 138.35 (2C), 135.44 (2C) (arom C), 129.47 (4C), 127.56 (4C) (arom CH), 112.41, 110.73 ($-\text{SCN}$), 71.29 ($>\text{C}=\text{}$), 46.40 ($-\text{CH}_2-$).

1,1-Bis(4-methoxyphenyl)-2-thiocyanatoethene (4d): colorless liquid; IR (cm^{-1}) 2160.26 ($-\text{SCN}$); ^1H NMR (CDCl_3 , δ , ppm) 7.25-6.84 (8H, m, arom H), 6.40 (1H, s, $=\text{CH}-$), 3.85, 3.80 ($-\text{OMe}$); ^{13}C NMR (CDCl_3 , δ , ppm) 160.24, 160.10, 132.30, 129.22 (arom C), 148.38 ($>\text{C}=\text{}$), 130.69 (2C), 128.87 (2C), 114.28 (2C), 113.94 (2C) (arom CH), 111.72 ($-\text{SCN}$), 107.87 ($=\text{CH}-$), 55.38, 55.35 ($-\text{OMe}$).

3. RESULTS AND DISCUSSION

3.1. Manganese(III)-Induced Reaction of 1,1-Diarylethenes with Potassium thiocyanate

First we prepared the starting materials, i.e. 1,1-diarylethene **1a-d**. Although these alkenes were not new compounds, their NMR spectra were recorded in order to use for the following elucidation of Mn(III)-induced reaction products. In an initial experiment of our second stage of this research, reaction of 1,1-diphenylethene (**1a**) with potassium thiocyanate (**2**), and manganese(III) acetate dihydrate with molar ratio of **1:2**:Mn(OAc)₃·2H₂O = 1:1.5:0.5 at 70 °C was performed. Surprisingly, the reaction completed within one minute and, after the work-up, allowed us to obtain 1,1-diphenyl-1,2-dithiocyanatoethane (**3a**) in 44 % isolated yield (scheme 1 and table 1, entry 1). Structure of product **3a** was established by spectroscopic methods. Its IR spectrum gave rise to a signal at 2158.43 cm^{-1} showing the presence of thiocyanate functional group in this compound. The ^1H NMR spectrum of **3a** simply consisted of aromatic hydrogen signal as a



a: Ar = Ph, b: Ar = 4-MeC₆H₄, c: Ar = 4-ClC₆H₄

Scheme 1: Reaction of 1,1-diarylethenes **1a-c** with potassium thiocyanate **2** in the presence of manganese triacetate dihydrate

multiplet at δ 7.45-7.23 and methylene signal as a singlet at δ 3.99. A comparison of the ¹³C NMR spectrum of **3a** with that of the starting material **1a** led to a conclusion that **3a** had no carbon-carbon double bond of alkene in its structure. It was worth noting that the ¹³C NMR spectrum of **3a** gave two signals at δ 111.16 and 111.13 (figure 1a) showing the presence of two thiocyanate groups in the molecule of this product. The above evidence strongly supported the fact that an addition reaction had occurred and **3a** was 1,1-diphenyl -1,2-dithiocyanatoethane.

In an attempt to improve the yield of **3a**, similar reactions at different molar ratios were examined (table 1, entries 2-5). The reaction of the molar ratio of **1**:**2**:Mn(OAc)₃·2H₂O = 1:4:2 resulted in a

significant improvement in product yield (69 %). Lowering the reaction temperature resulted in a slightly decreasing yield of **3a** (entries 6 and 7). Using an ethene containing electron-donating groups (**1b**) allowed us to collect the corresponding products **3b** in a higher yield (Entry 8). Meanwhile, an ethene having electron-withdrawing groups on its benzene rings (**1c**) slightly lowered its product yield (Entry 9) comparing to that of **1a**.

It was worth mentioning that, while two carbon signals of two thiocyanate groups of **3a** were too close that might give rise of certain concern about its determination (figure 1 a), both ¹³C NMR spectra of **3b** and **3c** showed two clearly separated peaks for two thiocyanate groups (figures 1b and 1c).

Table 1: Reaction of 1,1-diarylethenes **1a-c** with potassium thiocyanate in glacial acetic acid under the presence of manganese(III) acetate dihydrate

| Entry | Ethene | Molar ratio ^a | Reaction temperature (°C) | Reaction time (min.) | Product yield (%) ^b |
|-------|-----------|--------------------------|---------------------------|----------------------|--------------------------------|
| 1 | 1a | 1:1.5:0.5 | 70 | 1 | 3a (44) |
| 2 | 1a | 1:2:1 | 70 | 1 | 3a (45) |
| 3 | 1a | 1:3:1.5 | 70 | 1 | 3a (60) |
| 4 | 1a | 1:4:2 | 70 | 1 | 3a (69) |
| 5 | 1a | 1:4:3 | 70 | 1 | 3a (60) |
| 6 | 1a | 1:4:2 | 50 | 3 | 3a (67) |
| 7 | 1a | 1:4:2 | 23 | 15 | 3a (63) |
| 8 | 1b | 1:4:2 | 70 | 1 | 3b (78) |
| | 1c | 1:4:2 | 70 | 1 | 3c (65) |

^aThe molar ratio of **1**:**2**:Mn(OAc)₃·2H₂O. ^bIsolated yield based on the amount of 1,1-diarylethene used.

Because starting ethene **1b** produced product **3b** in very good yield (Entry 8), we next checked a similar reaction of ethene **1d** having more powerful electron-releasing groups, i.e. OMe instead of Me of **1b**. To our surprise, this reaction did not afford the expected addition product **3d** but 1,1-bis(4-methoxyphenyl)-2-thiocyanatoethene **4d** in excellent yield (scheme 2). The structure of this

product was confirmed by IR, ¹H NMR, ¹³C NMR and ¹³C DEPT spectra. The presence of an alkene carbon-carbon double bond was shown by two carbon signal at δ 148.38 (>C=) and 107.87 (=CH-) which were not much different from that of the starting material **1d** (148.90 (>C=), 111.63 (=CH₂)). One thiocyanate functional group gave rise at δ 111.72 (figure 1c).

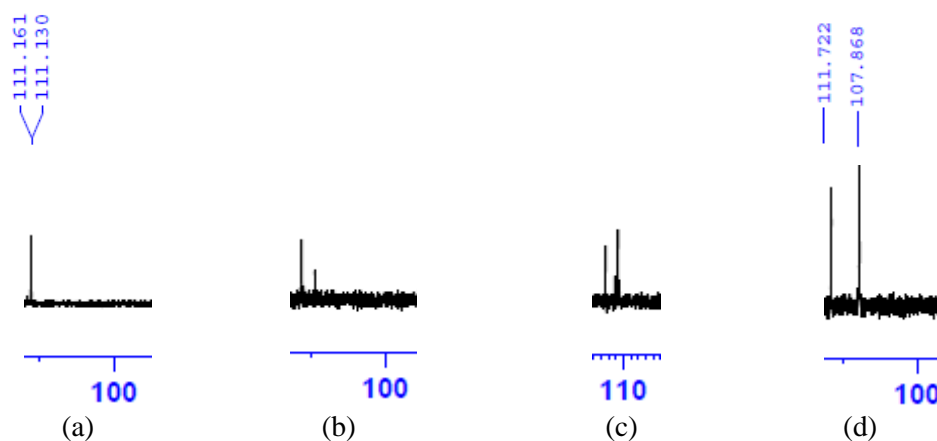
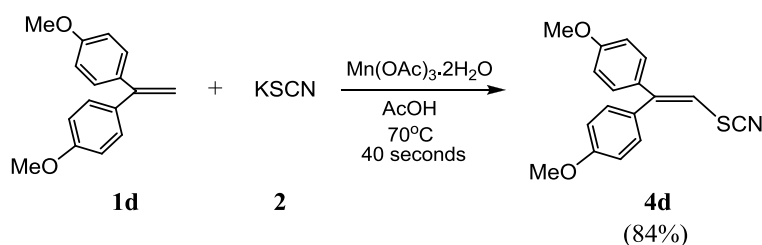


Figure 1: ^{13}C NMR spectra: (a), (b), and (c) Signals of two thiocyanate groups of **3a**, **3b**, and **3c**. (d) Signals of thiocyanate group and =CH- of **4d**

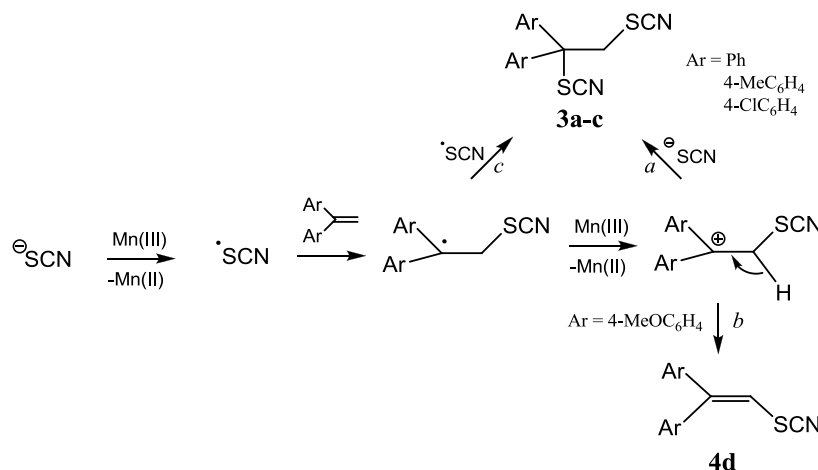


Scheme 2: Reaction of **1d** with potassium thiocyanate **2** in the presence of manganese triacetate dihydrate

3.2. Reaction mechanism

The reaction was thought to follow the radical mechanism described in Scheme 3. It was likely that the oxidation of thiocyanate anion by Mn(III) could form $\cdot\text{SCN}$ radical in the first step. Addition of this radical to an electron-rich alkene could produce a stable tertiary radical intermediate which then was further oxidized by Mn(III) to give the

corresponding carbocation. It seemed that, depending on the nature of substituents on benzene ring of the starting material, this carbocation might interact with thiocyanate anion to form **3** (in cases of **a-c**, path a) or go to a β -proton elimination step to produce **4** (in case of **d**, path b). We could say, reasonably enough, that the tertiary radical might interact with $\cdot\text{SCN}$ radical to afford product **3** before being further oxidized by Mn(III) (path c).



Scheme 3: Proposed mechanism for the formation of **3a-c** and **4d**

4. CONCLUSION

We have described a simple and straightforward method to the synthesis of dithiocyanates **3a-c** and thiocyanate **4d**. Furthermore, to our knowledge, there are no earlier reports on the synthesis of these compounds. We believe that this method will provide a useful method to existing ones for the synthesis of dithiocyanates, especially where very short reaction time is desired.

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