

Note

Formation of 5-phenyl-1,2-dithiole-3-thione from molybdenum dithiopropiolato complexes

Pradeep Mathur^{a,b,*}, Vidya D. Avasare^a, Abhijit K. Ghosh^a, Shaikh M. Mobin^b

^a Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076, India

^b National Single Crystal X-ray Diffraction Facility, Indian Institute of Technology, Powai, Bombay 400 076, India

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Abstract

Molybdenum dithiopropiolato complexes, $[(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Mo}(\text{CO})_2(\eta^2\text{-S}_2\text{CC}\equiv\text{CPh})]$ ($\text{R} = \text{H}$, $\text{R}' = \text{Me}$ **1a**, $\text{R} = \text{R}' = \text{H}$ **1b**; $\text{R} = \text{R}' = \text{Me}$ **1c**) react with trimethylamine-*N*-oxide (TMNO · 2H₂O) under mild thermolysis to form 5-phenyl-1,2-dithiole-3-thione (**2**). The reaction proceeds through the formation of the oxo-complexes, $[(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ ($\text{R} = \text{H}$, $\text{R}' = \text{Me}$ **3a**, $\text{R} = \text{R}' = \text{H}$ **3b**; $\text{R} = \text{R}' = \text{Me}$ **3c**). Direct reaction of **3a–c** with TMNO · 2H₂O under thermolysis also results in formation of **2**. © 2004 Elsevier B.V. All rights reserved.

Keywords: Dithiolethione; Molybdenum; Dithiopropiolato; Carbonyl; Oxo

1. Introduction

The 1,2-dithiole-3-thione and its derivatives are versatile compounds and find uses as chemoprotective agents [1,2] and for treatment of intestinal allergies and jaundice [3].

Although first isolated from *Brassica oleracea*, the synthesis of 1,2-dithiole-3-thione has been carried out by a variety of different methods, such as reaction of eugenol or isoeugenol with sulfur [4], reaction of $\text{ArCH}=\text{CHRR}'$ ($\text{Ar} = \text{phenyl}$ or anisole and $\text{R}, \text{R}' = \text{Me}$ or H) with sulfur [5,6]. The derivative, 5-phenyl-1,2-dithiole-3-thione (**2**) has been obtained from the reaction of $\text{PhCOCH}_2\text{CO}_2\text{Et}$ and P_4S_{10} [7–9]. Additionally, several other starting compounds such as β -ketodithioic acid and aryl ketones have been used for preparation of 1,2-dithiole-3-thione [10,11]. We have recently reported the preparation and crystal structures of some dithiopropiolato complexes, $[(\eta^5\text{-C}_5\text{R}_5)\text{Mo}(\text{CO})_2(\eta^2\text{-S}_2\text{CC}\equiv\text{CPh})]$ and their conversion to the oxo-derivatives $[(\eta^5\text{-C}_5\text{R}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ ($\text{R} = \text{H}$ or Me) by photolysis in presence of air [12]. In this paper, we report on the utility of the coordinated dithiopropiolato ligands in

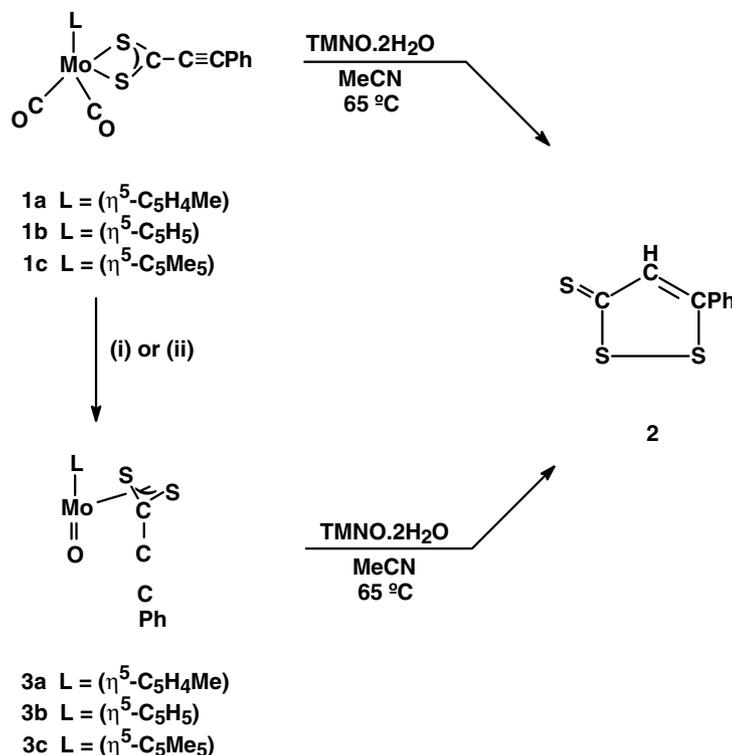
these complexes for the preparation of 5-phenyl-1,2-dithiole-3-thione.

2. Results and discussion

When an acetonitrile solution containing $[(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Mo}(\text{CO})_2(\eta^2\text{-S}_2\text{CC}\equiv\text{CPh})]$ ($\text{R} = \text{H}$, $\text{R}' = \text{Me}$ **1a**, $\text{R} = \text{R}' = \text{H}$ **1b**, $\text{R} = \text{R}' = \text{Me}$ **1c**) and 4 equivalents of hydrated trimethylamine-*N*-oxide (TMNO · 2H₂O) was heated at 65 °C, 5-phenyl-1,2-dithiole-3-thione (**2**) was obtained in yields of 80%, 33%, and 44%, respectively, as shown in Scheme 1. In the reaction using **1c**, the known oxo-compound, $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ (**3c**) was also isolated from the reaction mixture. When using **1a** and **1b**, we were unable to isolate the oxo-compounds, $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ from these reactions. To confirm whether the oxo-compounds, $[(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ could be intermediates in the formation of **2** from **1a–c**, we prepared the oxo-compounds $[(\eta^5\text{-C}_5\text{R}_4\text{R}')\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ ($\text{R} = \text{H}$, $\text{R}' = \text{Me}$ **3a**, $\text{R} = \text{R}' = \text{H}$ **3b**; $\text{R} = \text{R}' = \text{Me}$ **3c**) by photolysis of benzene solutions of **1a–c** under constant bubbling of air according to the method reported by us earlier [12]. Compound **2** was obtainable from the

* Corresponding author. Tel./fax: +91-222-572-4089.

E-mail address: mathur@chem.iitb.ac.in (P. Mathur).



Scheme 1. (i) TMNO·2H₂O, MeCN, 25 °C; (ii) benzene/air, *hν*, 0 °C.

oxo-compounds **3a–c** in yields of 83%, 47% and 43%, respectively, the best yields being obtained when acetonitrile solutions of **3a–c** and TMNO·2H₂O were heated at 65 °C. In an attempt to improve the yield of **2**, we investigated the reactions of **1a–c** and of **3a–c** with TMNO·2H₂O in the presence of sulfur powder. In both sets of reactions we did not observe any significant improvement in the yield of **2** formed (yield of **2** from reaction of **1a–c** with TMNO·2H₂O in presence of S: 84%, 38% and 47%, respectively; from reaction of **3a–c** with TMNO·2H₂O in presence of S: 86%, 50% and 42%, respectively).

Compound **2** was characterised on the basis of comparison of its IR and ¹H NMR spectroscopy with that reported earlier. Further, a single crystal X-ray structure determination established its molecular structure. The bond materials are in agreement with those reported earlier from a structure determination of the same compound [13] and, in general, bond distances in **2** are consistent with partial C–C and C–S double bond character.

Role of TMNO·2H₂O appears to be two fold in the overall sequence leading to formation of **2**. Firstly, it converts compounds **1a–c** to their respective oxo-forms. This has been independently established by us by isolating the oxo-compounds, [(η^5 -C₅R₄R')Mo(O)(η^3 -S₂CC≡CPh)] (**3a–c**) from the reactions of **1a–c** with TMNO·2H₂O (Scheme 1). Secondly, the water of hydration of TMNO serves as a source of proton to the central carbon

atom of the dithiolethione ring. When we used anhydrous TMNO, we did not observe formation of **2**.

3. Experimental

3.1. General considerations

Reactions and manipulations were carried out using standard Schlenk line techniques under an atmosphere of argon. Solvents were purified, dried and distilled under an argon atmosphere prior to use. Infrared spectra were recorded on a Nicolet Impact 400 FT IR spectrophotometer, as hexane solutions in 0.1 mm path length cells. ¹H NMR spectra were recorded on a Varian VXR-300S spectrometer in CDCl₃. Elemental analyses were performed using a Carlo–Erba automatic analyzer. Preparation of compounds [(η^5 -C₅R₄R')Mo(CO)₂(η^2 -S₂CC≡CPh)] (R = H, R' = Me **1a**, R = R' = H **1b**; R = R' = Me **1c**) and their conversion to the oxo-derivatives, [(η^5 -C₅R₄R')Mo(O)(η^3 -S₂CC≡CPh)] (R = H, R' = Me **3a**, R = R' = H **3b**; R = R' = Me **3c**) were carried out by the method reported earlier [12].

3.2. Preparation **2** from [(η^5 -C₅H₄Me)Mo(CO)₂(η^2 -S₂CC≡CPh)] **1a**

A solution of TMNO·2H₂O (41 mg, 0.37 mmol) in acetonitrile (50 ml) was added dropwise to an

acetonitrile solution (50 ml) of **1a** (30 mg, 0.074 mmol). The solution was subjected to constant heating at 65 °C for 45 min. After removal of the solvent the residue was re-dissolved in dichloromethane and filtered through Celite to remove insoluble material. The filtrate was concentrated and subjected to chromatographic work-up on silica gel TLC plates using hexane/dichloromethane (70/30 v/v) to yield a yellow band of **2** (8 mg, 80%).

Under identical conditions, compound **2** was obtained in yields of 33% and 44%, respectively from the reactions of **1b** and **1c**. Reaction of **1c** also yielded a second band during chromatographic work-up, orange $[(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ (**3c**) in 31% yield.

3.3. Preparation of **2** from $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{O})(\eta^3\text{-S}_2\text{CC}\equiv\text{CPh})]$ **3a**

A solution of $\text{TMNO} \cdot 2\text{H}_2\text{O}$ (13 mg, 0.12 mmol) in acetonitrile (15 ml) was added drop-wise to an acetonitrile solution (20 ml) of **3a** (11 mg, 0.029 mmol). The solution was subjected to constant heating at 65 °C under an atmosphere of argon for 45 min. After removal of the solvent the residue was re-dissolved in dichloromethane and filtered through Celite to remove insoluble material. The filtrate was concentrated and subjected to chromatographic work-up on silica gel TLC plates using hexane/dichloromethane (70/30 v/v) to yield a yellow band of **2** (3.5 mg, 83%).

Compound **2** was obtained in yields of 47% and 43% from the reaction of **3b** and **3c**, respectively, under identical conditions.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC No. 214070. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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