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

Abstract

Molybdenum dithiopropiolato complexes, [(η⁵-C₅R₄R₀)Mo(CO)₂(η²-S₂CC₆H₅)] (R = H, R₀ = Me 1a, R = R₀ = H 1b; R = R₀ = Me 1c) react with trimethylamine-N-oxide (TMNO•C₂H₂O) under mild thermolysis to form 5-phenyl-1,2-dithiole-3-thione (2). The reaction proceeds through the formation of the oxo-complexes, [(η⁵-C₅R₄R₀)Mo(O)(η²-S₂CC₆H₅)] (R = H, R₀ = Me 3a, R = R₀ = H 3b; R = R₀ = Me 3c). Direct reaction of 3a-c with TMNO•C₂H₂O under thermolysis also results in formation of 2.

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 ArCH=CHR′ (Ar = phenyl or anisole and R,R′ = Me or H) with sulfur [5,6]. The derivative, 5-phenyl-1,2-dithiole-3-thione (2) has been obtained from the reaction of PhCOCH₂CO₂Et and P₄S₁₀ [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, [(η⁵-C₅R₃)Mo(CO)₂(η²-S₂CC₆H₅)] and their conversion to the oxo-derivatives [(η⁵-C₅R₃)Mo(O)(η²-S₂CC₆H₅)] (R = 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 [(η⁵-C₅R₄R₀)Mo(CO)₂(η²-S₂CC₆H₅)] (R = H, R₀ = Me 1a, R = R₀ = H 1b, R = R₀ = Me 1c) and 4 equivalents of hydrated trimethylamine-N-oxide (TMNO•2H₂O) was heated at 65 ºC, 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, [(η⁵-C₅Me₅)Mo(O)(η²-S₂CC₆H₅)] (3c) was also isolated from the reaction mixture. When using 1a and 1b, we were unable to isolate the oxo-compounds, [(η⁵-C₅H₅Me)Mo(O)(η²-S₂CC₆H₅)] and [(η⁵-C₅H₅)Mo(O)(η²-S₂CC₆H₅)] from these reactions. To confirm whether the oxo-compounds, [(η⁵-C₅R₄R₀)Mo(O)(η²-S₂CC₆H₅)] could be intermediates in the formation of 2 from 1a-c, we prepared the oxo-compounds [(η⁵-C₅R₄R₀)Mo(O)(η²-S₂CC₆H₅)] (R = H, R₀ = Me 3a, R = R₀ = H 3b; R = R₀ = 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
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, [(η⁵-C₅H₄Me)Mo(O)(η³-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 [(η⁵-C₅R₄R')Mo(CO)₂(η³-S₂CC≡CPh)] (R = H, R' = Me 1a, R = R' = H 1b; R = R' = Me 1d) and their conversion to the oxo-derivatives, [(η⁵-C₅R₄R')Mo(O)(η³-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 [(η⁵-C₅H₄Me)Mo(CO)₂(η³-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 [(η⁵-C₅Me₅)Mo(O)(η²-S₂CC≡CPh)] (3c) in 31% yield.

3.3. Preparation of 2 from [(η⁵-C₅H₄Me)Mo(O)(η²-S₂CC≡CPh)] 3a

A solution of TMNO⋅2H₂O (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.

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References