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Synthesis and Physicochemical Properties of Methyl 3-Mercapto Arylpropene Dithioates

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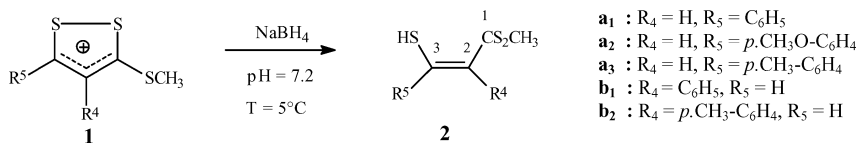
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Keywords Dimerization; dithiolethione; dithiolium; redox potential; sulfur-sulfur cleavage

INTRODUCTION

1,2-dithiole-3-thiones and derivatives are endowed with several promising pharmacological properties.¹ We have shown that the reduction of 3-(methylsulfanyl)-5-(phenyl)-1,2-dithiolium ion **1a₁** by NaBH₄ is an efficient way to prepare the corresponding reduction product: methyl-3-mercapto-3-phenylpropene dithioate **2a₁**.² We present here the generalization of this reaction to other 3-(methylsulfanyl)-1,2-dithiolium ions **1** to give methyl-3-mercapto-3-phenylpropene dithioates **2**. Compounds **2a₁** and **2a₂** have been previously described according to other synthetic routes.^{3,4}



SCHEME 1

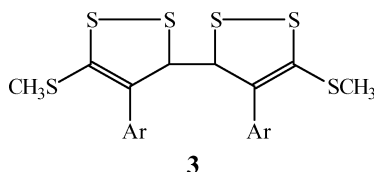
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RESULTS AND DISCUSSION

The 5-aryl derivatives (**1a**: $R_5 = \text{Ar}$) gave **2a** in very good yields (83–96%) conditionally operating at 5°C. The Z configuration of **2a₂** and its deprotonated form was deduced from two-dimensional NOESY spectra in CDCl_3 solvent. Compounds **2a** are oxidized by oxygen in basic and acidic solutions to give a mixture of unidentified products and the corresponding dithiolium cations, respectively.

Unlike 5-aryl derivatives, the reaction proceeded in a complicated way for 4-aryl derivatives (**1b**: $R_4 = \text{Ar}$). It gave a mixture of the expected dithioates and dimers **3**. The dimer **3b₁** was already isolated by electrolysis of 4-phenyl-1,2-dithiole-3-thione at platinum electrode after methylation.⁵ Purification attempts of the crude product on silica gel chromatography lead to dimers **3** whereas dithioates **2b** could not be isolated because of their high instability.



The cyclic voltammetry experiments in DMF/ Bu_4NPF_6 showed that **2a₂** is oxidized at a potential of $\text{Ep}^a = +0.61\text{V/ECS}$ to **1a₂** following a two-electron process: $\mathbf{2a_2} \rightleftharpoons \mathbf{1a_2} + 2\text{e}^- + \text{H}^+$. The redox couple **1a₂/2a₂** is electrochemically irreversible and chemically reversible. The pK_a value of $\mathbf{2a_2}/\mathbf{2a_2}^-$ was evaluated to 6.5 by calculation in H_2O ⁶ and to 9.4 in DMF.^{7,8} The anodic peak Ep^a of **2a₂** shifts on addition of $\text{Bu}_4\text{N}(\text{CH}_3\text{COO})_2$ ($\text{pK}_a(\text{CH}_3\text{CO}_2^-/\text{CH}_3\text{CO}_2\text{H}) = 14.2$ in DMF) as expected for proton-coupled electron transfer system.

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