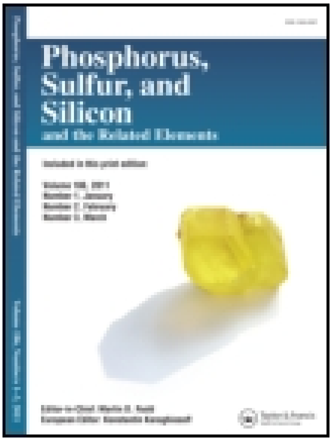

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Synthesis and Physicochemical Properties of Methyl 3-Mercapto Arylpropene Dithioates

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Synthesis and Physicochemical Properties of Methyl 3-Mercapto Arylpropene Dithioates

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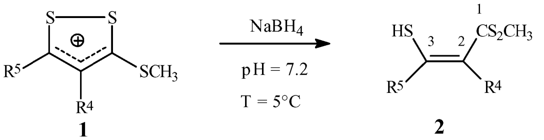
Keywords Dimerization; dithiolethione; dithiolium; redex potential; sulfur-sulfur cleavage

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 **1a**$_1$ by $NaBH_4$ is an efficient way to prepare the corresponding reduction product: methyl-3-mercapto-3-phenylpropene dithioate **2a**$_1$.[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 **2a**$_1$ and **2a**$_2$ have been previously described according to other synthetic routes.[3,4]



1 **2**

a$_1$: $R_4 = H, R_5 = C_6H_5$
a$_2$: $R_4 = H, R_5 = p.CH_3O\text{-}C_6H_4$
a$_3$: $R_4 = H, R_5 = p.CH_3\text{-}C_6H_4$
b$_1$: $R_4 = C_6H_5, R_5 = H$
b$_2$: $R_4 = p.CH_3\text{-}C_6H_4, R_5 = H$

SCHEME 1

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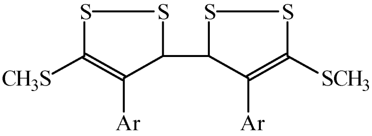
RESULTS AND DISCUSSION

The 5-aryl derivatives (**1a**: R_5 = Ar) gave **2a** in very good yields (83–96%) conditionally operating at 5°C. The Z configuration of $\mathbf{2a_2}$ 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 = Ar). It gave a mixture of the expected dithioates and dimers **3**. The dimer $\mathbf{3b_1}$ was already isolated by electrolysis of 4-phenyl-1,2-dithiole-3-thione at platinum electrode after methylation.[5] Purification attemps of the crude product on silica gel chromatography lead to dimers **3** whereas dithioates **2b** could not be isolated because of their high unstability.



3

The cyclic voltammetry experiments in DMF/Bu_4 NPF_6 showed that $\mathbf{2a_2}$ is oxidized at a potential of $Ep^a = +0.61$V/ECS to $\mathbf{1a_2}$ following a two-electron process: $\mathbf{2a_2} \rightleftharpoons \mathbf{1a_2} + 2e^- + H^+$. The redox couple $\mathbf{1a_2}/\mathbf{2a_2}$ is electrochemically irreversible and chemically reversible. The pKa 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 $\mathbf{2a_2}$ shifts on addition of $Bu_4N(CH_3COO)_2$ (pKa ($CH_3CO_2^-/CH_3CO_2H$) = 14.2 in DMF) as expected for proton-coupled electron transfer system.

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