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A. Oliva [a] , A. Molinari [a] & L. Sánchez [a]
[a] Instituto de Química, Universidad Católica de Valparaíso , casilla 4059, Valparaíso, Chile

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A New Application of Dimethyl Trithiocarbonate. Methylthiothiocarbonylation of 2,4-Pentanedione and Some β-Oxoesters.

Alfonso Oliva*, **Aurora Molinari and Lucía Sánchez**

Instituto de Química, Universidad Católica de Valparaíso, casilla 4059,
Valparaíso, Chile.

***Abstract**: 2,4-Pentanedione, ethyl acetoacetate, benzoyl acetate and diethyl malonate **1a-d** react with sodium acetate and dimethyl trithiocarbonate in dimethylformamide to afford methyl-β,β'-dicarbonyldithiocarboxylate derivatives **2a-d** in moderate yield.*

The condensation of active methylene compounds with carbon disulfide and alkyl halides in the presence of a base is well documented in the literature, and the reaction has been mostly focused on the preparation of ketene dithioacetals[1,2]. On the other hand, a carefully control in the stoichiometry of the added base allows to get the alkyl dithiocarboxylate derivative[3-6], but this is not a satisfactory general method for the preparation of this kind of compounds.

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*To whom correspondence should be addressed.

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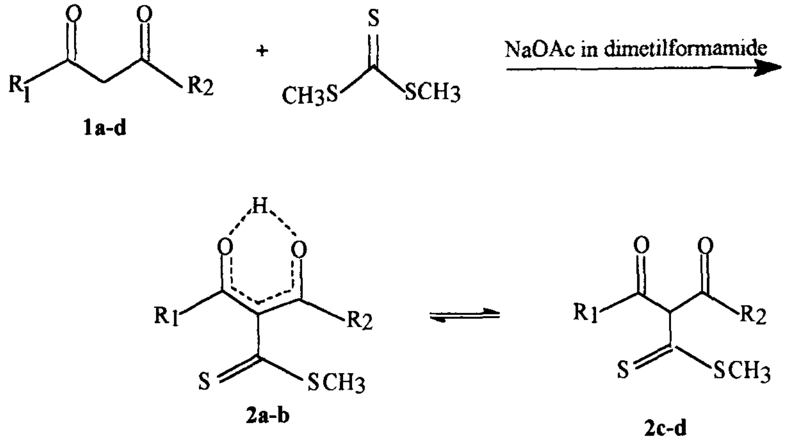
Another method for the preparation of alkyl dithiocarboxylates involves the condensation of active methylene derivatives with dialkyl trithiocarbonates in the presence of a base[7,8]. Thus, the reaction of substituted acetophenones with dimethyl trithiocarbonate and sodium hydride in boiling benzene affords methyl-3-oxo-3-arylpropanedithiocarboxylates and the reaction is also extended to cyclopentanone or cyclohexanone[9]. However, attempts to prepare dithiocarboxylates from ethyl cianoacetate, diethyl malonate or malononitrile by this method were not succesful. We wish to report in this communication, the preparation of methyl-β,β'-dicarbonyl dithiocarboxylates **2** by methylthiothiocarbonylation of β-dicarbonyl compound **1** with dimethyl trithiocarbonate using sodium acetate in dimethylformamide.

The reaction of 2,4-pentanedione **1a** with sodium acetate and dimethyltrithiocarbonate in dimethylformamide, affords methyl-2-acetyl-3-oxobutanedithiocarboxylate **2a** in moderate yield. Similarly, the dithiocarboxylates **2 b-d** are prepared from the β-oxoesters ethyl acetoacetate **1b,** benzoyl acetate **1c** and diethyl malonate **1d**, respectively.

All compounds were characterized by ^{1}H NMR, ^{13}C NMR and IR techniques. The ^{1}H NMR analysis of **2a** and **2b** in deuteriochloroform shows signals at 14.69 and 15.85 ppm respectively according with a enolic form[10], while methyne signals 6.20 and 5.20 observed in **2c** and **2d** are indicative of a un-enolized form. The ^{13}C NMR spectra in deuteriochloroform also confirm the enolic structure of **2a** and **2b**, observing the corresponding olefin carbon at 123.3 ppm and 91.2 ppm. Furthermore, the methyne carbon signal at 56.7 and 55.9 ppm for **2c** and **2d**, are also indicative of a un-enolized form.



	R_1	R_2
a	CH_3	CH_3
b	CH_3	OCH_2CH_3
c	Ph	OCH_2CH_3
d	OCH_2CH_3	OCH_2CH_3

EXPERIMENTAL

The NMR spectra were recorded at 200/50 MHz ($^1H/^{13}C$) in deuteriochloroform solutions with internal TMS on a Bruker AC-200 spectrometer and the chemical shifts are reported in ppm. The IR spectra were recorded on a Perkin Elmer FT IR 1600 in NaCl disc and the absorption frequencies are reported in reciprocal centimeters. Dimethyl trithiocarbonate was synthesized by a previously reported procedure[11].

General Procedure for Synthesis of Methyl-β,β'-dicarbonyl dithiocarboxylates (2a-d).

A mixture of β-dicarbonyl compound **1** (10 mmoles), sodium acetate (10 mmoles), dimethyl trithiocarbonate (10 mmoles) in dimethylformamide (10 ml) was stirred 24 hours at room temperature. After the addition of water (50 ml), the formed dithiocarboxylate was extracted with methylene chloride (4 x 25 ml). The organic layer was washed with 1.5 M hydrochloric acid (4 x 40 ml) and water (4 x 50 ml). The extract was dried with anhydrous sodium sulphate and evaporated to give the crude product **2**, which was purified by column chromatography on silica gel using hexane - ethyl acetate 4:1 as eluent.

Methyl-2-acetyl-3-oxobutanedithiocarboxylate (2a). This compound was prepared in 45% yield as a yellow oil ; IR ν C=O 1638 ; ^{1}H NMR ($CDCl_3$) δ 2.13 (s, 6H, CH_3), 2.71 (s, 3H, CH_3S), 14.69 (s, 1H, enolic OH). ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 23.1 (CH_3S), 123.3 (C-2), 188.8 (C=O), 206.0 (C=S).

Elemental analysis for $C_7H_{10}O_2S_2$ calculated: C 44.21, H 5.30, S 33.65; found : C 44.25, H 5.27, S 33.61.

Methyl-2-etoxicarbonyl-3-oxobutanedithiocarboxylate (2b). This compound was prepared in 42% yield as a orange oil ; IR ν 1734 (C=O), 1708 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, CH_3), 2.65 (s, 3H, CH_3), 2.73 (s, 3H, CH_3S), 4.17 (q, 2H, CH_2O), 15.85 (s, 1H, enolic OH). ^{13}C NMR ($CDCl_3$) δ 14.2 (CH_3), 23.2 (CH_3S), 30.3 ($\underline{C}H_3C$=O), 61.6 (CH_2O), 91.2 (C-2), 165.6 (O-C=O), 178.6 (C=O), 205.9 (C=S).

Elemental analysis for $C_8H_{12}O_3S_2$ calculated : C 43.63, H 5.50, S 29.06; found: C 43.68, H 5.45, S 28.95.

Methyl-2-etoxicarbonyl-3-oxo-3-phenylpropaneditiocarboxylate (2c). This compound was prepared in 40% yield as pale orange oil ; IR ν: 1704 (C=O), 1673 (C=O). ^{1}H NMR ($CDCl_3$) δ 1.23 (t, 3H, CH_3), 2.64 (s, 3H, CH_3S), 4.17 (q, 2H, CH_2O), 6.20 (s, 1H, CH), 6.90-8.20 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ 14.7 (CH_3), 23.7 (CH_3S), 56.7 (C-2), 61.3 (CH_2O 128.3-137.6 (Ph), 163.8 (O-C=O), 191.2 (C=O), 207.2 (C=S).

Elemental analysis for $C_{13}H_{14}O_3S_2$ calculated: C 55.31, H 5.00, S 22.67; found: C 55.28, H 5.03, S 22.61.

Methyl (bis-etoxicarbonyl) ethaneditiocarboxilate (2d). This compound was prepared in 46% yield as a pale yellow oil ; IR ν 1728 (C=O). ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 6H, CH_3), 2.63 (s, 3H, CH_3S), 4.17 (q, 4H, CH_2O), 5.20 (s, 1H, CH). ^{13}C NMR ($CDCl_3$) δ 14.7 (CH_3), 22.6 (CH_3S), 55.9 (C-2), 62.0 (CH_2O), 164.2 (O-C=O), 207.8 (C=S).

Elemental analysis for $C_9H_{14}O_4S_2$ calculated: C 43.19, H 5.64, S 25.57; found: C 43.24, H 5.58, S 25.65.

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