

# 4-(2-Hydroxyphenyl)-1,3-Dithiol-2-ylidene Derivatives

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*New 4-(2-hydroxyphenyl)-1,3-dithiol-2-ylidene derivatives have been synthesized from the reaction of the corresponding 4-(2-hydroxyaryl)-2-dialkylamino-1,3-dithiol-2-ylum perchlorate with various methylene active compounds under basic conditions. The newly obtained derivatives were characterized by NMR and MS spectrometry, UV-Vis and IR spectroscopy.*

**Keywords:** acetophenones, dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds

The formation of carbon-carbon bonds continues to receive a great deal of attention from the scientific community. Recent advances employ the use of metals as catalysts [1-4], as well as improvements of classical reactions like the Michael addition [5]. Heterocycles are an important resource for the material chemistry and not only. Amongst these, sulphur and nitrogen-containing heterocycles receive a great deal of attention [6-18]. These types of compounds have also biological applications [19-28].

For many years all the organic  $\delta$ -electron donors with conductivity properties were limited to the tetrachalcogenafulvalenes compounds [29-31]. Recently, the non-tetrachalcogenafulvalenes containing a 1,3-dithiol-2-ylidene based  $\pi$ -donor unity proved to give superconducting salts [32]. Moreover, novel dye-sensitized solar cells based on 1,3-dithiol-2-ylidene derivatives have been recently reported [33]. In general, charge-transfer [34-50] or push-pull [51-64] compounds have important applications in the field of conducting materials. An important precursor for 1,3-dithiol-2-ylidene derivatives are the 1,3-dithiolium-2-yl compounds [65, 66]. 1,3-Dithiolium salts contain a positive charge located at the C(2) position and consequently these systems are prone to nucleophilic interactions at this position [9, 67].

The synthesis of novel 4-(2-hydroxyphenyl)-1,3-dithiol-2-ylidene derivatives from the corresponding 1,3-dithiolium salts, via mesoionic compounds by the nucleophilic attack at the C(2) position of the 1,3-dithiolium ring, is reported.

## Experimental part

### Analysis methods

Melting points were obtained on a KSPI melting-point meter and are uncorrected. IR spectra were recorded on a

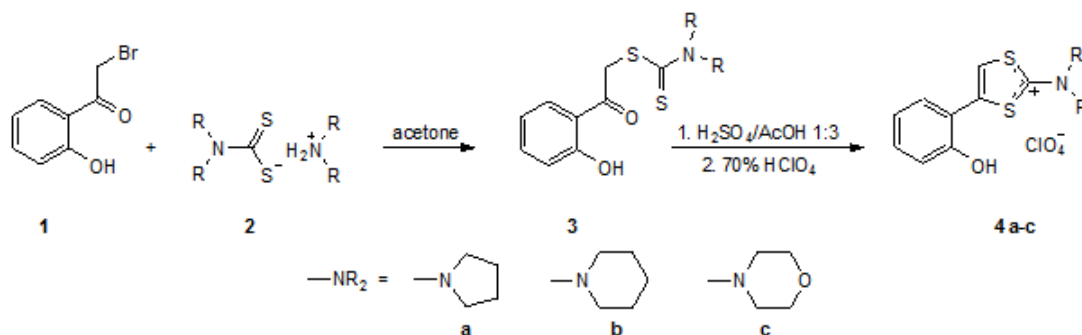
Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from TMS. UV-Vis spectra were recorded on a Varian BioChem 100 spectrophotometer. Mass spectra were recorded on a Thermo Scientific ISQ LT instrument. Elemental analyses (C, H, N and S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement ( $\pm 0.28\%$ ) with the calculated values.

### Synthesis

The reaction sequence for the synthesis of dithiocarbamate **3** and 1,3-dithiolium perchlorate **4** is described in Scheme 1 and were performed in accordance with the previously reported procedures [68-71]. 1,3-Dithiol-2-ylidene derivatives **6a-c** were synthesized under conditions described in scheme 2.

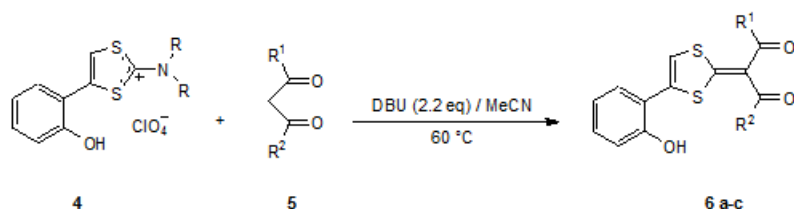
#### 1,3-Dithiol-2-ylidene derivative **6b**; General Procedure

To a suspension of 1,3-dithiolium perchlorate **4c** (0.38 g, 1mmol) in acetonitrile (15 mL) under nitrogen atmosphere, dimethylmalonate (**5b**, 0.16 mL, 1.05 mmol) and DBU (0.34 mL, 2.2 mmol) were added and the reaction mixture was brought to 60°C. The reaction mixture was left over night under stirring. The solution was then poured into water (100mL) and concentrated hydrochloric acid was added (3 mL). After stirring for 10 min, the precipitate that formed was filtered under vacuum and recrystallized from ethanol; yield 0.25 g (73%). The analytical and spectral data for the 1,3-dithiol-2-ylidene derivatives **6a-c** are presented in table 1.



Scheme 1. Synthesis of dithiocarbamate **3** and 1,3-dithiolium perchlorates **4**

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5, 6	R <sup>1</sup>	R <sup>2</sup>
<b>a</b>	CH <sub>3</sub>	CH <sub>3</sub>
<b>b</b>	OMe	OMe
<b>c</b>		

Scheme 2. Synthesis of 1,3-dithiol-2-ylidene derivatives **6a-c**

## Results and discussions

The main synthetic procedure for 1,3-dithiolium salts is represented by the acid catalyzed intramolecular cyclization of phenacyl carbodithioates [41-46]. A versatile synthesis of various salts of dithiocarbamic acid consists of reaction of secondary amine with carbon disulfide [68]. The reactions of these salts with *o*-bromophenones lead to various substituted phenacyl carbodithioates, under mild reaction conditions. Following this reaction pathway, 1-(2-hydroxyphenyl)-1-oxaethan-2-yl carbodithioates **3a-c** have been synthesized by reacting 2-bromo-1-(2-hydroxyphenyl)ethan-1-one (**1**) with pyrrolidinium pyrrolidine-1-carbodithioate (**2a**), piperidinium piperidine-1-carbodithioate (**2b**) and morpholinium morpholine-4-carbodithioate (**2c**), in acetone under heating (Scheme 1). Acid catalyzed cyclization of phenacyl carbodithioates **3a-c** provided the corresponding 1,3-dithiol-2-ylum cations, which were isolated as salts of perchloric acid **4a-c**. The analytical and spectral data of compound **3** and **4** are in agreement with those previously reported [69].

Due to the positive charge located at the C(2) position, 1,3-dithiol-2-ylum ring readily interact with nucleophiles [48]. In order to synthesize the target 1,3-dithiol-2-ylidene derivatives **6** we reacted 1,3-dithiolium perchlorates **4** with carbanions derived from various methylene active compounds **5** (scheme 2). In order to generate the C-nucleophiles we used 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base (but weak nucleophile) to extract a proton from the active methylene moiety. DBU is a strong enough base for this purpose and, due to the sterical hindrance, a weak nucleophile; this property avoid the nucleophilic

interaction with the 1,3-dithiolium ring as a competing reaction. The reactions have been performed in acetonitrile at 60°C, under nitrogen, providing 1,3-dithiol-2-ylidene derivatives in good to excellent isolated yields. The reactions have been performed using 2.2 eq. of DBU, in acetonitrile, at 60°C, under nitrogen, providing 1,3-dithiol-2-ylidene derivatives **6** in good isolated yields (table 1).

The formation of 1,3-dithiol-2-ylidene derivatives **6a-c** is supported by analytical and spectral data (table 1). IR spectroscopy indicates the presence of new carbonyl or ester bands, which originate from the active methylene compounds. <sup>1</sup>H NMR spectra reveals the presence of new methyl/methylene aliphatic signals for derivatives **6a-c**. It should be noted that the regeneration of the phenolic group is always indicated by the presence of a broad singlet at various chemical shifts depending on the nature of deuterated solvent. <sup>13</sup>C NMR spectra indicates the disappearance of the signal of the positively charged C(2) atom (ca. 185 ppm) and the appearance of the new signals corresponding to the new double bonded carbon atoms (ca. 175 ppm). Also, the new signals corresponding to the carbonyl groups and ester groups confirm the structures of the new 1,3-dithiol-2-ylidene derivatives. UV/VIS spectra also confirm the formation of 1,3-dithiolium-2-ylidene derivatives. A comparison between the precursor 1,3-dithiolium salt **4b** and 1,3-dithiolium-2-ylidene derivative **6c** shown the disappearance of the longest wavelength absorption band from **4b** (332 nm) and the appearance of a strong absorption band for the new double bond in compound **6c** (397 nm, fig. 1). A bathochromic shift of the

**Table 1**  
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOL-2-YLIDENE DERIVATIVES **6a-c**

	M.p., °C	η, %	Spectral data
<b>6a</b>	203-204	91	<sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ = 2.58 (6H, bs, 2CH <sub>3</sub> ); 6.89 (2H, m, Har-3 + H-5); 6.92 (1H, s, H-5); 7.27 (1H, m, Har-4); 7.56 (1H, m, Har-6); 10.12 (1H, bs, OH) ppm. <sup>13</sup> C NMR (CDCl <sub>3</sub> ): δ = 30.8, 30.9, 117.9, 119.1, 122.7, 124.5, 128.7, 131.0, 133.3, 134.8, 154.5, 173.4, 191.4, 191.6 ppm. FT-IR (ATR): ν = 1631, 1570, 1470, 1360, 1315, 720 cm <sup>-1</sup> . MS (EI): m/z = 308 (M <sup>+</sup> )
<b>6b</b>	219-220	73	<sup>1</sup> H NMR (DMSO- <i>d</i> <sub>6</sub> ): δ = 3.74 (3H, s, CH <sub>3</sub> ); 3.75 (3H, s, CH <sub>3</sub> ); 5.05 (1H, bs, OH); 6.88 (2H, m, Har-3 + H-5); 6.90 (1H, s, H-5); 7.24 (1H, m, Har-4); 7.53 (1H, m, Har-6) ppm. <sup>13</sup> C NMR (DMSO- <i>d</i> <sub>6</sub> ): δ = 52.3, 52.4, 117.9, 119.0, 122.5, 124.8, 128.9, 131.1, 133.6, 134.5, 154.4, 165.9, 166.0, 175.7 ppm. FT-IR (ATR): ν = 3345, 1629, 1388, 1279, 1011, 750, 740 cm <sup>-1</sup> . MS (EI): m/z = 340 (M <sup>+</sup> )
<b>6c</b>	191-192	85	<sup>1</sup> H NMR (CDCl <sub>3</sub> ): δ = 1.10 (6H, s, 2 CH <sub>3</sub> ); 2.57 (2H, s, CH <sub>2</sub> ); 2.58 (2H, s, CH <sub>2</sub> ); 6.87 (2H, m, Har-3 + H-5); 6.91 (1H, s, H-5); 7.21 (1H, m, Har-4); 7.53 (1H, m, Har-6); 9.89 (1H, bs, OH) ppm. <sup>13</sup> C NMR (CDCl <sub>3</sub> ): δ = 28.5, 30.9, 50.6, 50.7, 117.8, 118.6, 122.2, 124.8, 128.5, 130.3, 133.3, 134.7, 154.5, 173.3, 193.13, 193.15. FT-IR (ATR): ν = 1571, 1469, 1371, 744 cm <sup>-1</sup> . MS (EI): m/z = 348 (M <sup>+</sup> )

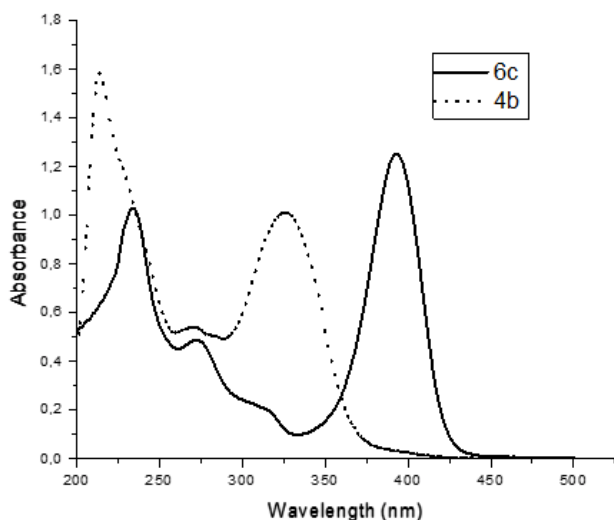


Fig. 1. UV/Vis absorption spectra of compounds **4b** and **6c** in ethanol

$\pi$ - $\pi^*$  absorption band from 214 nm in **4b** to 232 nm in **6c** was also observed.

## Conclusions

The synthesis of new 4-(2-hydroxyphenyl)-1,3-dithiol-2-ylidene derivatives has been performed by reacting the corresponding 1,3-dithiolium perchlorates with 2,4-pentandione, dimethylmalonate and dimedone. The methylene active compounds have been *in situ* converted into nucleophiles, using DBU, a non-nucleophilic base.

*Acknowledgments:* This work was supported by Ministry of Research and Innovation, CNCS - UEFISCDI, project number 152PED/2017 and project number PN-III-PI-I-PD-2016-1117, within PNCDI III. Authors thank SMIS-CSNR 13984-901, Project no. 257/2010, CERNESIM, for the NMR experiments.

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Manuscript received: 23.08.2018