Synthesis of Novel 4-(3,5-Dibromo-2-hydroxyphenyl)-5-Methyl-1,3-Dithiol-2-ylidene Derivatives

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Novel 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-1,3-dithiol-2-ylidene derivatives have been synthesized from the reaction of the corresponding 1,3-dithiol-2-ylium cations with various methylene active compounds. The 1,3-dithiol-2-ylium compounds have been obtained from the reaction of the substituted a-bromopropiophenone with various salts of dithiocarbamic acids. The newly obtained derivatives were characterized by NMR spectrometry and IR spectroscopy.

Keywords: dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds, propiophenones

The formation of carbon-carbon bonds continues to receive special attention from the scientific community. Recent advances employ the use of transition metals as catalysts [1-5], as well as improvements of classical reactions like the Michael addition [6]. Heterocycles are an important resource for the drug industry. Amongst these, sulphur and nitrogen-containing heterocycles receive a great deal of attention [7-23]. 1,3-Dithiolium salts contain a positive charge located at the C(2) position and for this reason these systems are well known for the reactivity of the C(2)-position towards nucleophiles [24]. The presence of a hydroxyphenyl moiety attached to the 1,3-dithiolium ring lead to a new class of mesoionic compounds on treatment with non-nucleophilic bases.

We are reporting here the synthesis of some new 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-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.

Experimental part

Analysis methods

Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker DPX-300 Spectrometer. Chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N, S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.29%) with the calculated values.

Synthesis

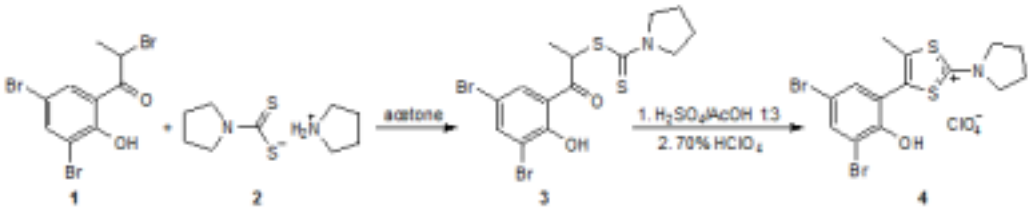
The reaction sequence for the synthesis of dithiocarbamate **3** and 1,3-dithiolium perchlorate **4** is described in scheme 1. 1,3-Dithiol-2-ylidene derivatives **7a-e** were accomplished using the reaction pathway presented in Scheme 2.

1-(3,5-Dibromo-2-hydroxyphenyl)-1-oxapropan-2-yl-pyrrolidine-1-carbodithioate (**3**)

To a solution of 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)propan-1-one (**1**, 1.935g, 5mmol) in acetone (50mL), a solution of pyrrolidinium pyrrolidine-1-carbodithioate (**2**, 1.1g, 0.005mol) in acetone-water (1:1, 20mL) was added. The reaction mixture was refluxed for 10min, cooled to room temperature and then poured into water. The precipitate was filtered, washed with water and dried off. Recrystallization from EtOH (50mL) gave colorless crystals; yield 1.9g (85%). M.p.=130-131°C. IR(ATR): 2935, 1642, 1429, 1309, 1244, 1112, 774, 670, 564 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.62 (3H, d, CH_3); 2.00 (2H, m, CH_2); 2.09 (2H, m, CH_2); 3.63 (2H, t, CH_2-N); 3.89 (2H, t, CH_2-N); 5.78 (1H, q, CH); 7.84 (1H, d, H-4); 8.19 (1H, d, H-6; J_{H4-H6}=2.2 Hz); 12.64 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$) δ : 16.1, 23.8, 25.2, 25.5, 43.1, 50.7, 52.5, 111.8, 113.5, 120.1, 131.5, 141.8, 158.7, 192.9, 202.5 ppm.

4-(3,5-Dibromo-2-hydroxyphenyl)-5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4**)

To a mixture of sulfuric acid (98%, 1mL) and glacial acetic acid (3mL), 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxapropan-2-yl-pyrrolidin-1-carbodithioate (**3**, 1g, 2.2mmol) was added in small portions. The reaction mixture was heated at 80 °C for 10min. After cooling, 70% $HClO_4$ (0.5mL) and then water (100mL) were added and the precipitate was filtered and dried off. Recrystallization from EtOH (100mL) gave colorless crystals; yield 0.85g (72%). M.p.=206-207°C dec. IR(ATR): 3048, 1547, 1425, 1211, 1085, 998, 872, 611, 550 cm^{-1}. ^1H NMR (DMSO-*d*6) δ : 2.23 (4H, m, $2CH_2$); 2.30 (3H, s, CH_3-5); 3.75 (4H, m,



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

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2CH_2); 7.44 (1H, d, H-4); 7.81 (1H, d, H-6; J_{H4-H6}=2.0 Hz); 10.11 (1H, s, OH) ppm. ^{13}C NMR (DMSO-*d*6) δ : 17.1, 25.2, 25.6, 56.4, 57.1, 112.5, 113.3, 118.2, 125.4, 133.2, 134.4, 137.5, 151.8, 185.6 ppm.

4,6-Dibromo-2-[5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5**)

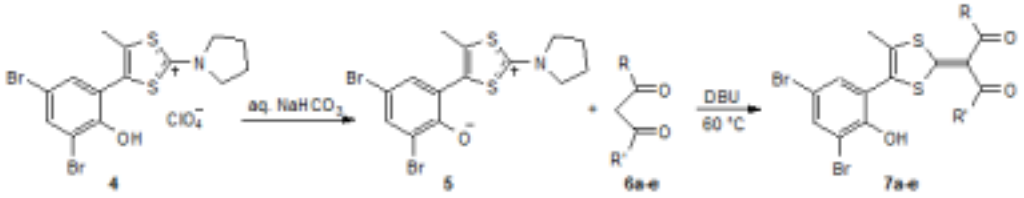
To a saturated sodium hydrogen carbonate solution (10mL), perchlorate **4** (0.535g, 1mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2 h under vigorous stirring at room temperature, the yellow solid was filtered off, washed with water, and dried. Recrystallization from ethanol gave yellow crystals; yield 0.435g (100%). M.p.=205-206°C dec. IR(ATR): 2965, 1514, 1425, 1211, 1137, 839, 709, 648 cm^{-1}. ^{1}H NMR (DMSO-*d*6) δ : 2.21 (4H, m, 2CH_2); 2.27 (3H, s, CH_3-5); 3.73 (4H, m, 2CH_2); 7.42 (1H, d, H-4); 7.78 (1H, d, H-6; J_{H4-H6}=2.0 Hz) ppm. ^{13}C NMR (DMSO-*d*6) δ : 17.7, 24.9, 25.3, 56.1, 57.1, 112.2, 113.1, 118.3, 125.7, 132.8, 134.9, 137.7, 151.5, 185.1 ppm.

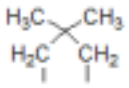
1,3-Dithiol-2-ylidene derivative **7a**; *General Procedure*

To a solution of mesoionic phenolate **5** (0.435g, 1mmol) in acetonitrile (15mL) under nitrogen atmosphere, 2,4-pentanedione (**6a**, 0.1mL, 1mmol) was added and the reaction mixture was brought to 60°C. DBU (0.17mL, 1.1mmol) was then added and the reaction was left over night under stirring. The solution was then poured into water (100mL) and concentrated hydrochloric acid was added (3mL). After stirring for 10 min , the precipitate that formed was filtered under vacuum and recrystalized from ethanol; yield 0.34g (72%). The spectral data for the 1,3-dithiol-2-ylidene derivatives **7a-e** are presented in table 1.

Table 1
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOL-2-YLIDENE DERIVATIVES **7a-e**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR, ppm
7a	150-151	72	2921, 2866, 1642, 1563, 1432, 1365, 1158, 953, 695	*^{1}H NMR* (CDCl$_3$) δ : 2.29 (3H, s, CH_3); 2.61 (6H, bs, 2CH_3); 6.67 (1H, bs, OH); 7.36 (1H, d, H-6; J_{H4-H6}=2.3Hz); 7.73 (1H, d, H-4). *^{13}C NMR* (CDCl$_3$) δ : 14.0, 30.9, 31.0, 112.3, 112.5, 120.4, 122.6, 130.7, 133.6, 135.6, 137.4, 150.0, 177.5, 192.2, 192.3 .
7b	232-233	75	1640, 1409, 1279, 1115, 790, 693, 544	*^{1}H NMR* (DMSO-*d*6) δ : 2.13 (3H, s, CH_3); 3.73 (3H, s, CH_3); 3.76 (3H, s, CH_3); 7.50 (1H, d, H-6; J_{H4-H6}=2.2 Hz); 7.87 (1H, d, H-4); 10.10 (1H, bs, OH). *^{13}C NMR* (DMSO-*d*6) δ : 14.2, 52.4, 100.7, 111.6, 113.7, 121.7, 128.5, 133.5, 135.4, 136.4, 152.1, 166.0, 166.1, 177.1 .
7c	121-122	80	2953, 1566, 1373, 862, 612, 567	*^{1}H NMR* (CDCl$_3$) δ : 1.08 (6H, s, 2 CH_3); 2.33 (3H, s, CH_3); 2.52 (2H, s, CH_2); 2.54 (2H, s, CH_2); 6.75 (1H, bs, OH); 7.37 (1H, d, H-6; J_{H4-H6}=2.3 Hz); 7.74 (1H, d, H-4). *^{13}C NMR* (CDCl$_3$) δ : 14.2, 28.5, 30.8, 50.5, 50.6, 112.4, 112.5, 116.8, 120.2, 130.6, 133.6, 135.8, 137.1, 150.1, 174.4, 193.1 .
7d	291-292	82	1633, 1579, 1485, 1446, 1209, 803, 657, 514	*^{1}H NMR* (DMSO-*d*6) δ : 2.24 (3H, s, CH_3); 7.58 (1H, d, H-6; J_{H4-H6}=2.3 Hz); 7.74 (4H, m); 7.90 (1H, s, H-6); 10.24 (1H, bs, OH). *^{13}C NMR* (DMSO-*d*6) δ : 14.5, 111.7, 113.4, 113.8, 121.2, 122.3, 122.4, 128.3, 133.5, 134.6, 135.8, 136.7, 140.0, 140.1, 152.2, 166.9, 186.9, 187.0 .
7e	183-184	71	2976, 2933, 1657, 1638, 1586, 1446, 1240, 1031, 944, 684	*^{1}H NMR* (CDCl$_3$) selected data for one isomer, δ : 1.43 (3H, t, CH_3); 2.26 (3H, s, CH_3); 2.83 (3H, s, CH_3); 4.39 (2H, q, CH_2); 7.15 (1H, d, H-6; J_{H4-H6}=2.3 Hz); 7.54 (1H, s, H-6); 12.32 (1H, bs, OH). *^{13}C NMR* (CDCl$_3$) selected data for one isomer, δ : 14.2, 14.3, 30.8, 60.5, 110.4, 116.5, 121.5, 121.6, 132.6, 133.8, 135.1, 159.4, 166.0, 166.5, 178.1, 192.0 .



6, 7	R	R'
a	CH_3	CH_3
b	OMe	OMe
c		
d		
e	CH_3	OEt

Scheme 2. Synthesis of 1,3-dithiol-2-ylidene derivatives **7a-e**

Results and discussions

The main synthetic procedure for 1,3-dithiolium salts is represented by the acid catalyzed intramolecular cyclization of phenacyl carbodithioates [25-30]. A versatile synthesis of various salts of dithiocarbamic acid consists of reaction of secondary amine with carbon disulfide [31]. The reactions of these salts with -bromophenones lead to various substituted phenacyl carbodithioates, under mild reaction conditions. Following this reaction pathway, 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxapropan-2-yl-pyrrolidine-1-carbodithioate (**3**) has been synthesized by reacting 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)propan-1-one (**1**) [32] with pyrrolidinium pyrrolidine-1-carbodithioate (**2**), in acetone under heating (scheme 1). This compound has been obtained as colorless crystals in 84% isolated yields. The structure of dithiocarbamate **3** has been proved by analytical and spectral data. The ^{1}H NMR spectra indicate a shift in value for the quartet belonging to the *a*-carbonyl proton from around 2.5ppm to 5.78ppm. Also, new signals appear at high fields (2.00, 2.09, 3.63 and 3.89) corresponding to the signals belonging to the the protons in pyrrolidine moiety. ^{13}C NMR spectra indicate the appearance of a new signal at 202.5ppm, attributed to the thiocarbonyl group.

As mentioned before, acid catalyzed cyclization of phenacyl carbodithioates provides the corresponding 1,3-dithiol-2-ylium cations. Thus, using a concentrated sulfuric acid-glacial acetic acid (1:3v/v) mixture, after 10min at 80°C a homogeneous reaction mixture that contains the 1,3-1,3-dithiol-2-ylium cation. In order to isolate a salt of this cation the reaction mixture was cooled to room temperature and 70% $HClO_4$ and water were added. Filtration and recrystallization of the precipitate gives 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4**) as colorless crystals, in 72% yield (scheme 1). The cyclization of carbodithioate **3** was accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (1642cm^{-1}) and the presence of new, strong and broad absorption bands at 998-1085cm^{-1}, corresponding to the perchlorate anion. Heterocyclization of carbodithioate **3** is also supported by the NMR spectra. Thus, the ^{1}H NMR spectra of 1,3-dithiol-2-ylium perchlorate indicate the absence of the *a*-carbonyl hydrogen from compound **3** (5.78ppm). ^{13}C NMR spectra also support the synthesis of 1,3-dithiolium salt **4** by the disappearance of the signals of carbonyl (192.9ppm) and thiocarbonyl (202.5ppm) carbon atoms present in the dithiocarbamate spectra and the appearance of a new signal at a very low field (185.6ppm) which correspond to the electron deficient C-2 atom.

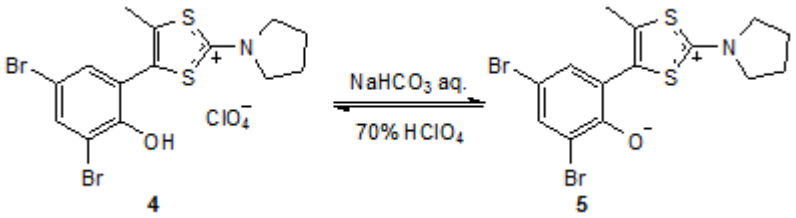
Treatment of 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4**), under heterogeneous conditions, with saturated aqueous sodium hydrogen carbonate solution provides 4,6-dibromo-2-[5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5**), in quantitative yields as yellow compounds (scheme 2). The presence of a hydroxy substituent in the *ortho*-position of the aryl substituent induces an extended delocalization of the negative charge up to the C4-C5 bond of the dithiol-2-ylium ring. In a previous paper [30], the comparative study of UV-Vis absorption spectra of 2-, 3-, and 4-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolates has shown that the yellow color of these zwitterionic compounds is due to a charge transfer between electron-rich and electron-deficient regions of the molecules and not to the contribution of quinoid structures in the ground states [33,34]. As mentioned before, phenolate **5** have been isolated as yellow products that present the features of mesoionic compounds [35]. The molecular structure of the new compound was proved by analytical and spectral data and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compound **5** with 70% $HClO_4$ regenerates the 1,3-dithiolium perchlorate **4** in quantitative yield (scheme 3).

Due to the positive charge located at the C(2) position, 1,3-dithiol-2-ylium ring is prone to nucleophilic attack [24]. In order to synthesize the target 1,3-dithiol-2-ylidene derivatives we reacted mesoionic phenolate **5** with carbanions derived from various methylene active compounds (scheme 2). In order to generate the *C*-nucleophiles we used 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base to extract a proton from the active methylene moiety. DBU is a strong enough base for this purpose and, do 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 (table 1).

In principle, the 1,3-dithiolium perchlorate **4** can be used instead of the corresponding mesoionic phenolate **5** in a one step procedure for reactions described in scheme 2. In that case, one extra equivalent of base is needed in order to convert, in a first step, the salt to mesoionic compound. However, DBU is much more expensive than sodium bicarbonate, therefore it is economically more feasible to use the latter to first convert the 1,3-dithiolium perchlorate into mesoionic phenolate, using the stepwise procedure.

A reasonable reaction mechanism has been previously proposed by us [36]. Most likely, the reaction mechanism involves two steps. The first one is represented by the nucleophilic attack of the *C*-nucleophile at the C(2) position of the 1,3-dithiolium ring; the C(2) carbon atom changes its hybridization from sp^2 to sp^3, this step being probably the fastest of the two. The second step involves the elimination of the pyrrolidine moiety and the formation of the double bond.

Once again, the formation of 1,3-dithiol-2-ylidene derivatives **7a-e** is supported by analytical and spectral data (table 1). IR spectroscopy indicates the presence of new carbonyl or ester bands, which come from the active methylene compounds. ^{1}H NMR spectra reveals the presence of new methyl/methylene aliphatic signals for derivatives **7a-e**. In the case of compound **7d**, a new multiplet can be found in the aromatic area, corresponding to the benzenic 1,3-indandione moiety. It should be noted



4 5

Scheme 3. The interconversion of mesoionic phenolate **5** with the corresponding 1,3-dithiolium perchlorate **4**

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. ^{13}C NMR spectra indicates the disappearance of the signal of the positively charged C(2) atom and the appearance of the new signals corresponding to the new double bonded carbon atoms. Also, the new signals corresponding to the carbonyl groups (ca. 192ppm) and ester groups (ca. 166ppm) confirm the structures of the new 1,3-dithiol-2-ylidene derivatives. It should be noted that compound **7e** has been obtained as a mixture of two isomers due to the asymmetry of ethyl acetoacetate. The spectral data are presented for one isomer.

Conclusions

The synthesis of new 4-(3,5-dibromo-2-hydroxyphenyl)-5-methyl-1,3-dithiol-2-ylidene derivatives has been performed by reacting the corresponding mesoionic substrate with various active methylene compounds. The latter have been *in situ* converted into nucleophiles, using DBU, a non-nucleophilic base. The newly obtained derivatives were characterized by NMR spectrometry and IR spectroscopy.

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