Synthesis of 2-Pyrrolydinyl-1,3-Dithiolium Derivatives from Propiophenones

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Novel bromo-substituted 4-(2-hydroxyaryl)-5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorates have been synthesized by the heterocondensation of the corresponding 1-(2-hydroxyaryl)-1-oxopropan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the corresponding substituted a-bromopropiophenones with pyrrolidinium pyrrolidine-1-carbodithioate. The mesoionic 4-(2-pyrrolidinyl-1,3-dithiol-2-ylium-4-yl)phenolates have been obtained from the corresponding 1,3-dithiolium perchlorates under weak basic conditions. These compounds were characterized by NMR and MS spectrometry, UV-Vis and IR spectroscopy.

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

The development of new organic superconductors is a major topic in the field of molecular conductors [1]. Since the discovery of the metallic conductivity in a tetrathiafulvalene-tetracyanoquinodimethane complex [2] tetrachalcogenafulvalenes have played a leading role in the development of new molecular metals and superconductors [3-5]. In general, charge-transfer [6-12] or push-pull [13-29] compounds have important applications in the field of conducting materials. For these reasons heterocyclic compounds - especially those containing sulfur and nitrogen - represent an important resource for the material chemistry [30-39] and not only (biologically active compounds, daily life and even the educational process) [40-52]. Recent studies on (1,3-dithiolium-2-yl)phenolates systems revealed that 1,3-dithiolium cations can act as acceptor groups in intramolecular charge-transfer processes [6,8,53,54].

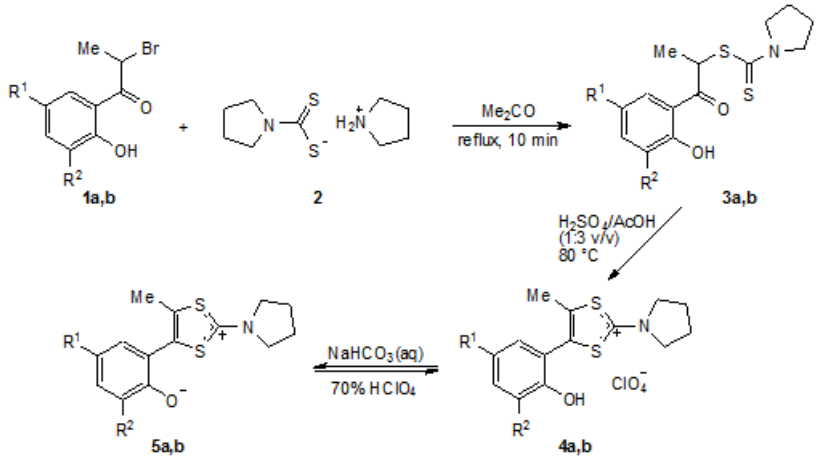
Following our previous investigation on the synthesis of some 4-(hydroxyaryl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts from the corresponding *a*-haloketones [55,56], we wish to extend these studies by presenting new bromo-substituted 4-(2-hydroxyaryl)-5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiolium perchlorates and the corresponding mesoionic 2-(5-methyl-1,3-dithiolium-2-yl)phenolates.

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 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, S) were conducted using a CE440 Elemental Analyzer; the results were found to be in good agreement (±0.30%) with the calculated values.

Synthesis



1, 3, 4, 5	R^1	R^2
a	Br	H
b	Br	Br

Scheme 1. Synthesis of dithiocarbamates **3**, 1,3-dithiolium perhlorates **4** and mesoionic phenolates **5**

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1-(5-Bromo-2-hydroxyphenyl)-1-oxopropan-2-yl-pyrrolidine-1-carbodithioate (**3a**)*; General Procedure*

To a solution of 2-bromo-1-(5-bromo-2-hydroxyphenyl) propan-1-one (**1a**, 1.54g, 5mmol) in acetone (15mL), a solution of pyrrolidinium pyrrolidine-1-carbodithioate (1.1g, 5mmol) in acetone-water (1:1, 15mL) was added. The reaction mixture was refluxed for 10 min, cooled to room temperature and then poured in water. The precipitate was filtered, washed with water and dried off. Recrystallization from EtOH (25mL) gave colorless crystals. Yield 1.38g (74%); mp 90-91°C. ^{1}H NMR ($CDCl_3$): δ = 1.59 (3H, d, CH_3), 2.02 (4H, m, $2CH_2$), 3.75 (2H, m, CH_2-N), 3.81 (2H, m, CH_2-N), 5.78 (1H, q, CH), 6.90 (1H, d, H-3), 7.53 (1H, dd, H-4; J_{H3-H4}=7.9 Hz), 8.11 (1H, d, H-6, J_{H4-H6}=2.4 Hz), 11.95 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.5, 24.3, 26.1, 43.3, 51.2, 55.8, 110.7, 119.3, 120.6, 132.6, 139.2, 161.8, 192.3, 203.0 ppm. FT-IR (ATR): ν = 2980, 1644, 1441, 1319, 1245, 1213, 1128, 847, 774, 672 cm^{-1}. MS (EI): *m/z* = 373 (24%, M^+ for $C_{14}H_{16}{}^{79}BrNO_2S_2$).

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

White solid; 0.4g (85%); mp 130-131°C. ^{1}H NMR ($CDCl_3$): δ= 1.60 (3H, d, CH_3), 2.06 (4H, m, $2CH_2$), 3.78 (2H, m, CH_2-N), 3.82 (2H, m, CH_2-N), 5.77 (1H, q, CH), 7.86 ($1H_{ar}$, d, H-4, J_{H4-H6}=2.3 Hz), 8.14 ($1H_{ar}$, d, H-6, J_{H4-H6}=2.3 Hz), 12.62 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.1, 24.4, 26.2, 50.9, 51.2, 55.1, 110.8, 113.3, 119.7, 131.8, 141.6, 158.4, 193.6, 202.8 ppm. FT-IR (ATR): ν = 2964, 1646, 1439, 1320, 1239, 1218, 1130, 850, 783, 678, 541 cm^{-1}. MS (EI): *m/z* = 451 (20%, M^+ for $C_{14}H_{15}{}^{79}Br_2NO_2S_2$).

4-(5-Bromo-2-hydroxyphenyl)-5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4a**); *General Procedure*

To a mixture of sulfuric acid (98%, 1.1mL) and glacial acetic acid (3.3mL), 1-(3-bromo-2-hydroxyphenyl)-1-oxopropan-2-yl-pyrrolidine-1-carbodithioate (**3a**, 1.12g, 3mmol) was added in small portions. The reaction mixture was heated at 80°C for 10 min. After cooling, 70% $HClO_4$ (0.5mL) and then water (50mL) were added and the precipitate was filtered and dried off. Recrystallization from EtOH (20mL) gave colorless crystals. Yield 1.23g (90%); mp 214-215°C. ^{1}H NMR (DMSO-d_6): δ= 2.19 (4H, m, $2CH_2$), 2.29 (3H, s, CH_3-5), 3.71 (4H, m, $2CH_2$), 6.98 (1H, d, H-3), 7.52 (2H, m, H-4+H-6), 10.84 (1H, bs, OH) ppm. ^{13}C NMR (DMSO-d_6): δ = 15.4, 26.6, 57.0, 57.1, 110.7, 117.9, 118.9, 127.7, 133.1, 133.8, 135.0, 155.5, 179.3 ppm. FT-IR (ATR): ν= 3048, 1552, 1421, 1248, 1065, 868, 608, 549 cm^{-1}. MS (EI): *m/z* = 356 (8%, M^+-ClO_4 for $C_{14}H_{15}{}^{79}BrNOS_2$).

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

White solid; 0.85g (72%); mp 206-207°C dec. ^{1}H NMR (DMSO-d_6): δ = 2.18 (4H, m, $2CH_2$), 2.23 (3H, s, CH_3-5), 3.83 (4H, m, $2CH_2$), 7.56 ($1H_{ar}$, d, H-4, J_{H4-H6}=2.3 Hz), 7.92 ($1H_{ar}$, d, H-4, J_{H4-H6}=2.3 Hz), 10.54 (1H, bs, OH) ppm. ^{13}C NMR (DMSO-d_6): δ= 15.3, 26.4, 56.8, 56.9, 111.7, 113.9, 120.0, 126.0, 133.6, 133.9, 137.4, 152.4, 184.1 ppm. FT-IR (ATR): ν= 3049, 1551, 1438, 1248, 1095, 995, 871, 621, 548 cm^{-1}. MS (EI): *m/z* = 434 (7%, M^+ for $C_{14}H_{14}{}^{79}Br_2NOS_2$).

4-Bromo-2-[5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5a**)*;*
General Procedure

To a saturated sodium hydrogen carbonate solution (20mL), perchlorate **4a** (0.5g, 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 *N,N*-dimethylformamide gave a yellow solid. Yield 0.39g (100%); mp 223-224°C dec. ^{1}H NMR (DMSO-d_6): δ= 2.18 (4H, m, $2CH_2$), 2.40 (3H, s, CH_3-5), 3.69 (4H, m, $2CH_2$), 6.94 (1H, d, H-3), 7.42 (2H, m, H-4+H-6) ppm. ^{13}C NMR (DMSO-d_6): δ = 15.3, 26.4, 57.1, 57.2, 110.6, 118.0, 118.9, 127.5, 133.2, 133.8, 135.2, 155.6, 179.7 ppm. FT-IR (ATR): ν = 2938, 1547, 1494, 1448, 1243, 1131, 838, 709, 658 cm^{-1}.

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

Yellow solid; 0.32g (100%); mp 205-206°C. ^{1}H NMR (DMSO-d_6): δ = 2.17 (4H, m, $2CH_2$), 2.24 (3H, s, CH_3-5),

Empirical formula	$C_{14}H_{15}Br_2NO_2S_2$	
Formula weight	453.21	
Temperature	100(2) K	
Wavelength	1.54184 A	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.10129(18) Å	α= 90°
	b = 12.17644(9) Å	β= 109.3854(11)°
	c = 14.77336(15) Å	γ = 90°
Volume	3241.27(5) Å^3	
Z	8	
Density (calculated)	1.857 Mg/m^3	
Absorption coefficient	8.784 mm^{-1}	
F(000)	1792	
Crystal size	0.22 x 0.16 x 0.15 mm^3	
Theta range for data collection	4.38 to 76.17°	
Index ranges	-24<=h<=24, -15<=k<=15, -17<=l<=18	
Reflections collected	47374	
Independent reflections	3389 [R(int) = 0.0567]	
Completeness to theta = 76.17°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.63631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3389 / 0 / 194	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0212, wR2 = 0.0576	
R indices (all data)	R1 = 0.0224, wR2 = 0.0586	
Largest diff. peak and hole	0.363 and -0.574 e.Å^{-3}	

Table 1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR **3b**

3.83 (4H, m, $2CH_2$), 7.53 ($1H_{ar}$, d, H-4, J_{H4-H6}=2.2 Hz), 7.91 ($1H_{ar}$, d, H-4, J_{H4-H6}=2.2 Hz) ppm. ^{13}C NMR (DMSO-d_6): δ = 15.4, 26.5, 56.81, 56.86, 111.6, 113.8, 120.1, 126.0, 133.4, 133.8, 137.7, 152.1, 184.5 ppm. FT-IR (ATR): ν= 2941, 1548, 1492, 1441, 1244, 1139, 845, 721, 658 cm^{-1}.

*X-ray Structure Determination of **3b**:*

Numerical details are presented in Table 1 [57].

The intensity data of **3b** was collected on a Stoe IPDS 2T diffractometer with MoK_a radiation. The data were collected with the Stoe XAREA program using *w*-scans [58]. The space groups were determined with the XRED32 program [58]. The structures were solved by direct methods (SHELXS-97) and refined by full matrix least-squares methods on F^2 using SHELXL-97 [59,60].

Results and discussions

Phenacyl carbodithioates are important intermediates for the synthesis of 1,3-dithiolium salts and of their derivatives. The reactions of *a*-bromophenones with salts of dithiocarbamic acid, readily available from the reaction of secondary amine with carbon disulfide [61], represent the synthetic way to various substituted phenacyl carbodithioates. Following this synthetic strategy, we obtained phenacyl dithiocarbamates **3a**,**b** by reacting pyrrolidinium pyrrolidine-1-carbodithioate with 2-bromo-1-(5-bromo-2-hydroxyphenyl)propan-1-one (**1a**) [62,63] and 2-bromo-1-(3,5-dibromo-2-hydroxyphenyl)propan-1-one (**1b**) [64]. These compounds have been obtained as colorless crystals in good isolated yields (74, 85%). The structure of dithiocarbamates **2** has been proved by analytical and spectral data. The ^1H NMR spectra indicate a shift in value for the quartet belonging to the *a*-carbonyl proton from around 2.5 ppm to ca. 5.77 ppm. Also, new signals appear at high fields corresponding to the signals belonging to the rest of the protons in the pyrrolidine moieties. ^{13}C NMR spectra indicate the appearance of a new signal at 192-193 ppm, attributed to the thiocarbonyl group. The structure of 1-(3,5-dibromo-2-hydroxyphenyl)-1-oxopropan-2-yl-pyrrolidine-1-carbodithioate (**3b**) has unambiguously proved by X-ray crystallography (fig. 1). Crystal data are presented in table 1. The recorded data confirms the extended *p*-π conjugation at the level of dithiocarbamic group [65,66]; the length of N-C(10) bond is 1.323(2) Å, shorter than N-C(11) and N-C(14) that are essentially π-bonds (1.47(2) Å). The dihedral angle between the plane of the phenol group and that of the planar section of the pyrrolidine-1-carbodithiolate moiety is 108.07(12) °.

Using a concentrated sulfuric acid-glacial acetic acid (1:3 v/v) mixture [55,63,64] the cyclization of dithiocarbamates **3a**,**b** takes place under mild reaction conditions. After 10 min at 80°C the homogeneous reaction mixture was cooled to room temperature and 70% $HClO_4$ and water were added. Filtration and recrystallization of the precipitate gives perchlorates **4** as colorless crystals, in good yields. The cyclization of dithiocarbamates **3** was accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1645 cm^{-1}) and the presence of new, strong and broad absorption bands at 1100-1200 cm^{-1}, corresponding to the perchlorate anion. Heterocyclization of dithiocarbamates **3** is also supported by the NMR spectra. Thus, the ^1H NMR spectra of 1,3-dithiol-2-ylium perchlorate indicate the disappearance of the quartet of *a*-carbonyl hydrogen atom from compounds **2** (ca. 5.7 ppm). ^{13}C NMR spectra also support the synthesis of 1,3-dithiolium salts **4** by the disappearance of the carbonyl and thiocarbonyl carbon atoms present in the dithiocarbamates spectra and the appearance of a new signal at a very low field (180-184 ppm) which correspond to the electron deficient C-2 atom.

Treatment of perchlorates **4a**,**b** under heterogeneous conditions, with saturated aqueous sodium hydrogen carbonate solution provides bromo-substituted 2-[5-methyl-2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolates **5a**,**b** in quantitative yields as yellow compounds (Scheme 1). This is a reversible process that regenerates the 1,3-dithiolium perchlorates **4** in quantitative yields by treatment of an acetone suspension of the mesoionic compounds **5** with 70% $HClO_4$.

The presence of a hydroxy substituent in the *ortho*- or *para*-positions induces an extended delocalization of the negative charge up to the C4-C5 bond of the dithiolium ring. In a previous paper [6], 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. As mentioned before, phenolates **5** have been isolated as yellow products that present the features of mesoionic compounds [67]. The yellow color of mesoionic phenolates **5a**,**b** is also provided by an intramolecular charge transfer, that was proved by measurement of UV-Vis absorption spectra at different concentrations.

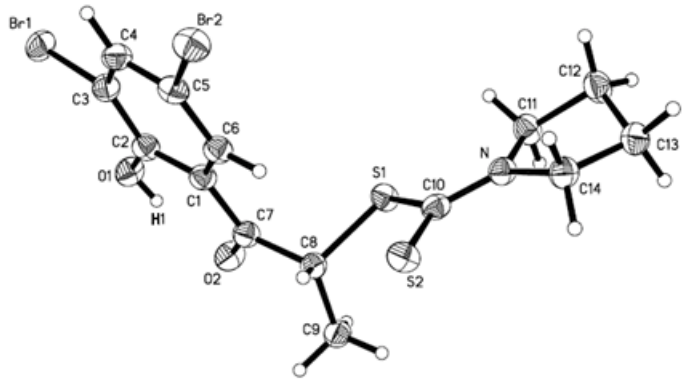

Fig. 1. Molecular structure of compound **3b**. Ellipsoids represent 50% probability levels. Selected molecular dimensions (Å,°): N-C(10) 1.323(2), S(1)-C(10) 1.7966(16), S(2)-C(10) 1.6679(18), N-C(10)-S(2) 124.34(12), N-C(10)-S(1) 111.98(12), S(2)-C(10)-S(1) 123.68(10)

Conclusions

The synthesis of several 4-(2-hydroxyaryl)-5-methyl-2-(*N*-pyrrolidine)-1,3-dithiol-2-ylium derivatives has been accomplished by the heterocyclization of the corresponding phenacyl carbodithioates derived from propiophenone. Crystallographic data revealed an extented *p-δ* conjugation at the level of dithiocarbamic group of compound **3b**. The structure of the new compounds has been proved by analytical and spectral (NMR, IR, UV-Vis, MS) data.

Acknowledgments: CNCS - UEFISCDI support within PNCDI III is acknowledged by LGS and LGB for project numbers PN-III-Pl-l.1-PD-2016-0962 and PN-III-Pl-l.1-PD-2016-1117, respectively. Romanian Ministry of Research and Innovation support within the Program 1 - Development of the national RD system, Subprogram 1.2 - Institutional Performance – RDI excellence funding projects, Contract no. 34PFE/ 19.10.2018 is acknowledged by LGS. Authors thank SMIS-CSNR 13984-901, Project no. 257 / 2010, CERNESIM, for the NMR experiments.

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Manuscript received: 9.09.2018