New Evidence for the Mesoionic Character of 2-(1,3-dithiol-2-ylium)phenolates

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New evidence for the mesoionic character of 2-(1,3-dithiol-2-ylium)phenolates have been obtained from bromination reactions of the 1,3-dithiolium ring. Bromination at the 5th position indicates an extended delocalization of the negative charge. The resulted 1,3-dithiolium bromides were converted in the corresponding mesoionic phenolates under weak basic conditions. The brominated mesoionic phenolates exhibit internal charge transfer.

Keywords: 1,3-dithiolium salts, mesoionic compounds, internal charge transfer

Mesoionic compounds are dipolar five or six membered heterocyclic compounds in which both the negative and the positive charge are delocalized; they cannot be satisfactorily represented by Lewis structures not involving charge separation. This implies a certain degree of aromatic character (in terms of [4*n* + 2] electrons) in the positively charged ring, which is counterbalanced by a negatively charged exocyclic atom [1]. One important category of mesoionic derivatives was discovered by Earl and Mackney in 1935 and named *sydnones* according to the name of the city [2]. Since then, a large variety of mesoionic compounds were disclosed. Between them, sulfur and nitrogen-containing heterocyclic compounds have maintained the continuous interest of researchers [3-16]. One such report highlighted the synthesis of various substituted 2-(1,3-dithiol-2-ylium)phenolates, named *iasinones*, again according to the name of a Romanian city [17]. Of special interest are systems where the donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety [18, 19]. In this context, investigations on a series of (1,3-dithiolium-2-yl)phenolates showed that 1,3-dithiolium ions can also serve as an acceptor moiety in intramolecular charge-transfer systems [20]. We wish to report here new evidence for the mesoionic character of *iasinones* obtained from bromination reactions of several 2-(1,3-dithiol-2-ylium)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 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 (±0.3%) with the calculated values.

Synthesis

2-[2-(*N*,*N*-Dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **1a-e**, 4-bromo-2-[2-(*N*,*N*-dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **2a-e** [8], and 4,6-dibromo-2-[2-(*N*,*N*-dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **3a-e** [10] were brominated with the corresponding amount of molecular bromine in order to provide 5-bromo-1,3-dithiol-2-ylium bromides **4a-e**, in good isolated yields (fig.1).

*5-Bromo-4-(3,5-dibromo-2-hydroxyphenyl)-2-(N,N-diethylamino)-1,3-dithiol-2-ylium bromide (**4b**); General Procedure*

Method A: To a solution of phenolate **1b** (1g, 3.7mmol) in glacial acetic acid (50mL) a solution of bromine (0.58mL, 11mmol) in glacial acetic acid (2mL) was added dropwise at rt. A precipitate was formed, that was filtered off, washed with water, and dried. Recrystallization from ethanol (50mL) gave colorless crystals; yield 1.4 g (64%). Analytical and spectral data of 1,3-dithiolium bromides **4** are presented in table 1.

Method B: To a solution of phenolate **2b** (1g, 2.9mmol) in glacial acetic acid (50mL) a solution of bromine (0.3mL, 5.8mmol) in glacial acetic acid (2mL) was added dropwise at rt. A precipitate was formed, that was filtered off, washed with water, and dried. Recrystallization from ethanol (45mL) gave colorless crystals; yield 1.1 g (65%). Analytical and spectral data of 1,3-dithiolium bromides **4** are presented in table 1.

Method C: To a solution of phenolate **3b** (1g, 2.3mmol) in glacial acetic acid (50mL) a solution of bromine (0.12mL, 2.3mmol) in glacial acetic acid (2mL) was added dropwise at rt. A precipitate was formed, that was filtered off, washed with water, and dried. Recrystallization from ethanol (40mL) gave colorless crystals; yield 0.88 g (64%). Analytical and spectral data of 1,3-dithiolium bromides **4** are presented in table 1.

*4,6-Dibromo-2-[5-bromo-2-(N,N-diethyl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5b**);*

To a saturated sodium hydrogen carbonate solution (20mL), bromide **4b** (1g, 1.71mmol) was added. Carbon dioxide evolved and the reaction mixture became yellow. After 2 h under vigorous stirring at room temperature, the

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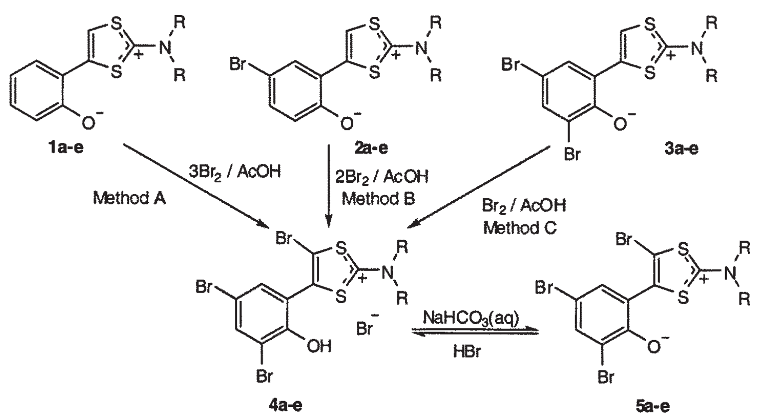

Fig. 1. Synthesis of 5-bromo-1,3-dithiol-2-ylium bromides **4** and of corresponding mesoionic phenolates **5**

1, 2, 3, 4, 5	R	R
a	CH_3	CH_3
b	CH_2CH_3	CH_2CH_3
c	$(CH_2)_4$	
d	$(CH_2)_5$	
e	$(CH_2)_2$-O-$(CH_2)_2$	

Table 1

ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM BROMIDES **4**

	M.p., °C	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
4a	240-241 dec.	3044, 1579, 1440, 1302, 851, 621, 575	^{1}H *NMR* δ : 3.85 (3H, s, CH_3); 3.92 (3H, s, CH_3); 5.20 (1H, s, OH); 7.53 (1H, d, H-4); 7.80 (1H, d, H-6; J_{H4-H6}= 2.1 Hz). ^{13}C *NMR* δ : 46.8, 47.1, 107.2, 111.5, 113.6, 119.3, 130.1, 133.4, 137.5, 152.3, 184.9
4b	201-202 dec.	3061, 1571, 1441, 865, 781, 622, 577	^{1}H *NMR* δ : 1.43 (3H, t, CH_3); 1.46 (3H, t, CH_3); 3.95 (2H, q, CH_2); 4.04 (2H, q, CH_2); 4.91 (1H, s, OH); 7.49 (1H, d, H-4′); 7.76 (1H, d, H-6; J_{H4-H6}= 2.2 Hz). ^{13}C *NMR* δ : 10.8, 10.9, 53.8, 54.1, 107.1, 111.4, 113.8, 119.4, 130.2, 133.5, 137.9, 152.5, 184.6
4c	209-210 dec.	3059, 1569, 1438, 624, 563	^{1}H *NMR* δ : 2.22 (4H, m, $2CH_2$); 3.65 (2H, t, CH_2-N); 3.76 (2H, t, CH_2-N); 5.60 (1H, s, OH); 7.52 (1H, d, H-4); 7.84 (1H, d, H-6; J_{H4-H6}= 2.2 Hz). ^{13}C *NMR* δ : 26.4, 26.9, 56.8, 57.1, 107.5, 111.3, 113.9, 119.5, 130.0, 133.5, 137.8, 152.4, 185.1
4d	228-229 dec.	3081, 1555, 1438, 1257, 855, 619, 571	^{1}H *NMR* δ : 1.77 (6H, m, $3CH_2$); 3.89 (4H, m, $2CH_2$-N); 5.60 (1H, s, OH); 7.55 (1H, d, H-4); 7.88 (1H, d, H-6; J_{H4-H6}= 2.1 Hz). ^{13}C *NMR* δ : 21.4, 24.9, 25.1, 56.5, 57.9, 107.2, 111.1, 113.7, 119.3, 130.1, 133.4, 137.2, 152.1, 185.0
4e	192-193 dec.	3060, 1551, 1433, 1260, 881, 620, 549	^{1}H *NMR* δ : 3.94 (8H, m, $4CH_2$); 5.58 (1H, s, OH); 7.54 (1H, d, H-4); 7.86 (1H, d, H-6; J_{H4-H6}= 2.1 Hz). ^{13}C *NMR* δ : 53.1, 53.2, 65.0, 107.1, 111.4, 113.2, 119.2, 130.6, 133.3, 137.1, 152.4, 185.2

Table 2

ANALYTICAL AND SPECTRAL DATA OF MESOIONIC 1,3-DITHIOLIUM PHENOLATES **5**

	M.p., °C	IR-ATR, cm^{-1}	NMR (DMSO-*d6*)
5a	201-202 dec.	2985, 1561, 1511, 1462, 1261, 1131, 866, 801, 711, 660	^{1}H *NMR* δ : 3.87 (6H, s, $2CH_3$); 7.51 (1H, d, H-4); 7.77 (1H, d, H-6; J_{H4-H6}= 2.1 Hz). ^{13}C *NMR* δ : 47.3, 47.8, 104.9, 115.0, 117.3, 118.8, 122.4, 129.7, 135.6, 160.5, 185.3
5b	193-194 dec.	2977, 1553, 1509, 1459, 1264, 1239, 1130, 859, 714, 661, 562	^{1}H *NMR* δ : 1.44 (6H, t, $2CH_3$); 3.92 (2H, q, CH_2); 3.99 (2H, q, CH_2); 7.48 (1H, d, H-4); 7.75 (1H, d, H-6; J_{H4-H6}= 2.1 Hz). ^{13}C *NMR* δ : 10.5, 10.6, 51.5, 53.2, 104.8, 115.1, 117.1, 118.7, 122.5, 129.8, 135.8, 160.6, 185.1
5c	201-202 dec.	3001, 1549, 1494, 1460, 1267, 1130, 857, 806, 657, 556	^{1}H *NMR* δ : 2.21 (4H, m, $2CH_2$); 3.63 (2H, t, CH_2-N); 3.72 (2H, t, CH_2-N); 7.50 (1H, d, H-4); 7.80 (1H, d, H-6; J_{H4-H6}= 2.2 Hz). ^{13}C *NMR* δ : 26.1, 26.3, 56.4, 56.8, 104.7, 115.3, 117.5, 118.9, 122.6, 129.9, 135.7, 160.4, 185.3
5d	205-206 dec.	3011, 1544, 1498, 1461, 1275, 1131, 860, 805, 660, 570	^{1}H *NMR* δ : 1.76 (6H, m, $3CH_2$); 3.88 (4H, m, $2CH_2$-N); 7.52 (1H, d, H-4); 7.84 (1H, d, H-6; J_{H4-H6}= 2.2 Hz). ^{13}C *NMR* δ : 21.7, 25.0, 25.1, 56.4, 57.6, 104.6, 115.5, 117.8, 119.1, 122.5, 129.7, 135.5, 160.6, 185.1
5e	250-251 dec.	2944, 1555, 1501, 1457, 1255, 1148, 850, 714, 661, 562	^{1}H *NMR* δ : 3.92 (8H, m, $4CH_2$); 7.51 (1H, d, H-4); 7.84 (1H, d, H-6; J_{H4-H6}= 2.1 Hz). ^{13}C *NMR* δ : 54.0, 54.5, 64.8, 104.8, 115.7, 117.9, 119.5, 122.3, 129.8, 135.5, 160.3, 185.1

yellow solid was filtered off, washed with water, and dried. Recrystallization from DMF gave yellow crystals; yield 0.86 g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **5** are presented in table 2.

Results and discussions

As previously reported by us, the synthesis of phenolates **1a-e**, **2a-e**, and **3a-e** has been accomplished by the heterocyclization of the corresponding phenacyl carboditioates, followed by treatment of resulted 1,3-dithiol-2-ylium salts with weak bases. During investigations on interconversion possibilities of phenolates **1a-e**, **2a-e**, and **3a-e**, we disclosed that bromination of unsubstituted phenolates **1a-e** occurs on both benzene and 1,3-dithiol ring. The same positions were substituted when phenolates **2a-e** were used as substrates. Moreover, bromination of phenolates **3a-e** takes place exclusively at the C5 position of the 1,3-dithiol ring and this step appears to be the fastest one when compared with the time for total bromination of **1a-e** and **2a-e**. The NMR spectra support the bromination

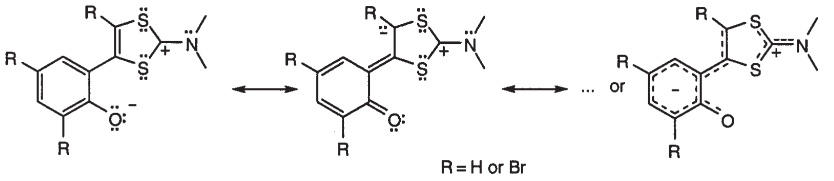

Fig. 2. Extended delocalization charge in mesoionic phenolates

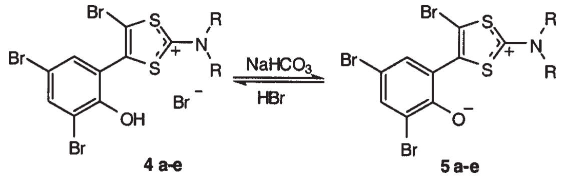

Fig. 3. Synthesis of mesoionic phenolates **5**

of phenolates **1-3**. The structure of 1,3-dithiolium bromides **4a-e** has been proved by analytical and spectral data (table 1).Thus, the ^{1}H NMR spectra of the 1,3-dithiol-2-ylium bromides indicate the absence of the signal for the hydrogen atoms from the C5 of the 1,3-dithiolium ring and appearance of pattern of a meta substituted aromatic core.

While bromination of the benzene core proceeded by classical electrophilic substitution, the bromination of the 1,3-dithiolium ring revealed new insights on the structural features of the investigated phenolates. While a nucleophilic substitution of the C5 is practically impossible under these working conditions, the mechanism for the substitution must be an electrophilic one. This implies an extended delocalization of the negative charge of the phenolate to the C5 atom, as described in figure 2. According to this structural characterization, these compounds present the features of mesoionic compounds [21, 22].

Treatment of bromides **4a-e**, under heterogeneous conditions, with saturated aqueous sodium hydrogencarbonate solution provides [2-(dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **5a-e**, in quantitative yields (fig. 3). The molecular structure of the new compounds was proved by analytical and spectral data (table 2) and by the following chemical transformation: treatment of an acetone suspension of the mesoionic compounds **5** with HBr regenerates the 1,3-dithiolium bromides **4** in quantitative yields.

These compounds were isolated as yellow crystalline products. The interconversion between mesoionic phenolates **5** and 1,3-dithiolium salts was also confirmed by UV-Vis absorption spectra. Deprotonation of the 1,3-dithiolium salts is accompanied by the appearance of a new absorption band at 407 nm, associated with the yellow color of these compounds. As previously reported by us [20], the absorption band at 407 nm originates from an internal charge transfer between electron-rich and electron-deficient regions of the molecules. The comparative study of the spectra of 1,3-dithiolium bromides **4** and phenolates **5** indicates that both structures exhibit the same absorption bands at 215 nm and 325 nm, corresponding to the $\pi \rightarrow \pi^*$ transition of the aromatic core and $n \rightarrow \pi^*$ for the electron deficient area, respectively. However, mesoionic phenolates **5** present a new absorption band at 240 nm that corresponds to the contribution of the quinoid form to the ground state.

Conclusions

New evidences for the mesoionic character of 2-(1,3-dithiol-2-ylium)phenolates have been obtained from bromination reactions of the 1,3-dithiolium ring. Bromination at the 5th position indicates an extended delocalization of the negative charge. The resulted 1,3-dithiolium bromides were converted in the corresponding mesoionic phenolates under weak basic conditions. UV-Vis investigations of the reported compounds revealed the presence of an internal charge transfer in the mesoionic phenolates, which is responsible for their yellow color.

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