ACTA CHEMICA IASI, **19**, 125-135 (2011)

Synthesis of Iodine Containing Mesoionic 2-(1,3-Dithiolium)phenolates

Laura G. Sarbu and Lucian M. Birsa *

Departament of Chemistry, "Al.I. Cuza" University Iasi, 11 Carol I Bd, Iasi 700506, Romania

Abstract: New mesoionic iodine containing 2-(1,3-dithiolium)phenolates have been synthesized by heterocyclocondensation of the corresponding dithiocarbamates followed by basic hydrolysis.

Keywords: Dithiocarbamates; 1,3-Dithiolium salts; Mesoionic compounds.

Introduction

The remarkably fast development of the 1,3-dithiolium salts chemistry over the past decade has been prompted by several factors. These compounds are hetero analogs of tropylium cation. Secondly, the ability of *S*-containing heterocycles to give charge-transfer complexes with suitable acceptors has provided the additional stimulus for the study of such structure since the complexes obtained exhibit metal-like conductivity in quite a large number of cases.[1] On the other hand, solvatochromic dyes have played an important role in the understanding of solvent polarity effects and are increasingly important as probes of complex biological systems.[2-4] The systems where a donor moiety is linked through a σ- or π-bonded bridge to the acceptor moiety received special interest.[5] A variety of acceptor units

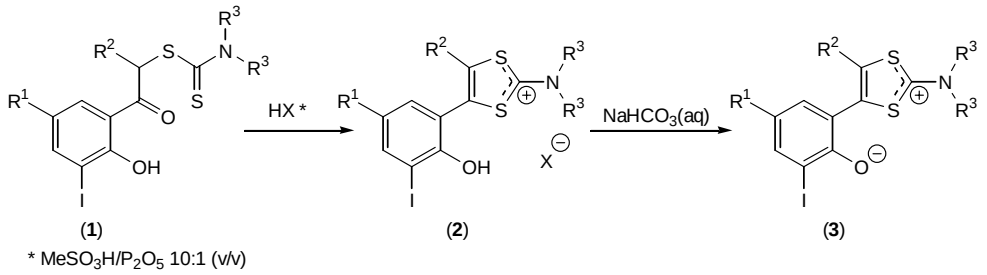
* Dr. Lucian M. Birsa, tel: +40 232 201349, fax: +40 232 201313, e-mail: lbirsa@uaic.ro

have been investigated with special attention paid to cationic systems, such as pyridinium and bipyridinium cations.[6-8]

In a previous paper we reported a new and mild method for the cyclization of iodine containing dithiocarbamates by using a $MeSO_3H$: P_2O_5 (10:1) mixture.[9] In order to extend the investigations on the synthesis of new iodine containing 1,3-dithiolium derivatives we wish to report the synthesis of a series of mesoionic 2-(1,3-dithiolium)phenolates.

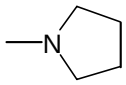
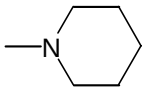
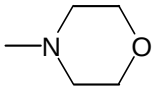
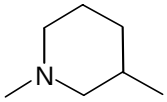
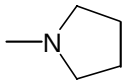
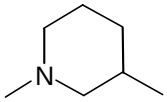
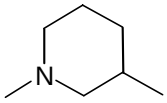
Results and Discussion

The synthesis of 2-dialkylamino-1,3-dithiolium salts is well-known in the literature.[10, 11] The most used method consists in heterocyclocondensation of the corresponding dithiocarbamates.[12, 13] The synthetic sequence of the target compounds is described in Scheme 1. Phenacyl *N*,*N*-dialkyldithiocarbamates **1a**–**h** have been prepared by reaction of the corresponding *ω*-bromo-ketones with various *N*,*N*-dialkyldithiocarbamates. However, special experimental conditions must be used for sensitive precursors. Typical cyclization agents have failed to provide the desired 1,3-dithiolium salts. Using a P_2O_5 – $MeSO_3H$ (1:10) mixture as cyclization agent[9] proved to be a proper way to obtain 1,3-dithiolium salts (**2**) as pure compounds and in high yields. Furthermore, we have found that the cyclocondensation takes place in high yields even at room temperature. Thus, a suspension of (**1**) in three parts of the ‘‘superacid’’ mixture was stirred at room temperature for 30 min to give a solution, which contained the corresponding 1,3-dithiolium cation. In some cases addition of 70% perchloric acid and methyl acetate to this solution give perchlorates (**2a**), (**2e**), and (**2h**) as white crystalline products.



(**1**) (**2**) (**3**)

* $MeSO_3H/P_2O_5$ 10:1 (v/v)

Compound	R^1	R^2	$N(R^3)_2$
(1a), **(2a)**, **(3a)**	I	H	$-NEt_2$
(3b)	I	H	
(3c)	I	H	
(3d)	I	H	
(1e), **(2e)**, **(3e)**	I	H	
(1f), **(3f)**	I	Me	
(1g), **(3g)**	I	Me	
(1h), **(2h)**, **(3h)**	Me	Et	

Scheme 1

Treatment of salts (**2**) under heterogeneous conditions, with saturated aqueous potassium hydrogencarbonate solution affords 2-(1,3-dithiol-2-ylium-4-yl)phenolates (**3a-h**), in quantitative yields. These

compounds were isolated as yellow crystalline products that present the features of mesoionic compounds.[14-16] The presence of a hydroxy substituent in an *ortho*-position induces an extended delocalization of the negative charge up to the C(4)-C(5) bond of the dithiolium ring.

The cyclization of phenacyl carbodithioates **1** to the corresponding mesoionic phenolates was accompanied by significant changes in the spectral features. The IR spectra revealed the disappearance of the carbonyl absorption band from the region of 1625 - 1635 cm^{-1}. Nuclear magnetic resonance spectra also indicated that the heterocyclocondensation has occurred through the disappearance of the signal for aliphatic hydrogens (4.7 - 4.9 ppm) and for compounds **3a-e** the appearance of a new signal at lower field (*ca.* 8 ppm) for the C(5) proton of 1,3-dithiolium ring.

Conclusions

The synthesis of iodine containing mesoionic 2-(1,3-dithiolium)phenolates has been reported by heterocyclocondensation of the correponding phenacyl carbodithioates. The reactions have been performed in the presence of a P_2O_5 – $MeSO_3H$ (1:10) mixture as cyclization agent.

Acknowledgements

This work was supported by CNCSIS –UEFISCSU, projects number PNII – IDEI 2095/2008.

Experimental

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 the CE440 Elemental Analyser; their results were found to be in good agreement (±0.25%) with the calculated values. Mass spectra were recorded on a Finnigan MAT 90X spectrometer. The synthesis of compounds **1b-d** and **2b-d** has been previously reported by us.[9]

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxoethan-2-yl-diethylamino-1-carbodithioate (**1a**)*; General Procedure*

To a solution of 2-bromo-1-(2-hydroxy-3,5-diiodophenyl)ethan-1-one (4.7 g, 0.01 mol) in acetone (30 mL) a solution of sodium *N*,*N*-diethylamino-1-carbodithioate·$3H_2O$ (2.29g, 0.01 mol) in acetone-water (1:1, 30 mL) was added. After 5 min under stirring at rt the precipitate was filtered, washed with water and dried off. Recrystallization from dioxane (50 mL) gave colorless crystals; yield 2.83 g (53%).

Mp 161-162 °C. IR (ATR): 2850, 1638, 1430, 1325, 1237, 1148, 950, 851, 650 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.16 (t, 3H, CH_3), 1.27 (t, 3H, CH_3), 3.82 (q, 2H, CH_2), 3.93 (q, 2H, CH_2), 4.93 (s, 2H, CH_2), 8.23 (d, ^4J = 2.3 Hz, 1H, H_{ar}), 8.39 (d, ^4J = 2.3 Hz, 1H, H_{ar}), 12.42 (s, 1H, OH). MS (ESI): *m/z* = 535 (M^+).

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxoethan-2-yl-(3-methylpiperidine)-1-carbodithioate (**1e**):

Yield 72%. Mp 182-183 °C. IR (ATR): 2920, 1641, 1445, 1320, 1208, 1142, 973, 848, 769, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 (d, 3H, CH_3), 1.23 (m, 1H, H-3), 2.15 (m, 4H, 2 H-4 + 2 H-5), 2.90 (m, 1H, H-2), 3.22 (m, 1H, H-6), 4.48 (m, 1H, H-2), 4.99 (s, 2H, CH_2), 5.20 (m, 1H, H-

6), 8.31 (d, ^4J = 2.4 Hz, 1H, H_{ar}); 8,44 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 12.08 (s, 1H, OH). MS (ESI): *m/z* = 561 (M^+).

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxopropan-2-yl-pyrrolidine-1-carbodithioate (**1f**):

Yield 85%. Mp 149-150 °C. IR (ATR): 2970, 1630, 1415, 1351, 1238, 1199, 1148, 758, 690 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.55 (d, 3H, CH_3), 2.01 (m, 4H, $2CH_2$), 3.61 (t, 2H, CH_2-N), 3.90 (t, 2H, CH_2-N), 5.79 (q, 1H, CH), 8.19 (d, 1H, H_{ar}), 8.35 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 12.79 (s, 1H, OH). MS (ESI): *m/z* = 547 (M^+).

1-(2-Hydroxy-3,5-diiodophenyl)-1-oxopropan-2-yl-(3-methylpiperidine)-1-carbodithioate (**1g**):

Yield 71%. Mp 157-158 °C. IR (ATR): 2864, 1636, 1430, 1314, 1231, 1155, 941, 850, 682 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, 3H, CH_3-3), 1.22 (m, 1H, H-3), 1.57 (d, 3H, CH_3-2), 1.75 (m, 4H, 2H-4 + 2H-5), 2.83 (m, 1H, H-2), 3.16 (m, 1H, H-6), 4.37 (m, 1H, H-2); 5.17 (m, 1H, H-6), 5.79 (q, 1H, H-2), 8.19 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 8.31 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 12.72 (s, 1H, OH). MS (ESI): *m/z* = 575 (M^+).

1-(2-Hydroxy-3-iodo-5-methylphenyl)-1-oxobutan-2-yl-(3-methylpiperidine)-1-carbodithioate (**1h**):

Yield 65%. Mp 104-105 °C. IR (ATR): 2890, 1645, 1414, 1321, 1228, 1111, 991, 680 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.95 (d, 3H, CH_3), 1.00 (t, 3H, CH_3), 1.22 (m, 1H, H-3), 1.75 (m, 4H, 2H-4 + 2H-5), 2.00 (m, 2H, CH_2), 2,28 (s, 3H, CH_3), 2.84 (m, 1H, H-2), 3.15 (m, 1H, H-6″), 4.37 (m, 1H, H-2), 5.18 (m, 1H, H-6), 5.83 (t, 1H, H-2), 7.79 (d, ^4J = 2.4 Hz, 1H,

H_{ar}), 7.84 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 12.75 (s, 1H, OH). MS (ESI): *m/z* = 477 (M^+).

2-Diethylamino-4-(2-hydroxy-3,5-diiodophenyl)-1,3-dithiol-2-ylium perchlorate (**2a**); *General Procedure*

To a mixture of P_2O_5–CH_3SO_3H (1:10, 3 mL) carbodithioate **1a** (0.53 g, 1 mmol) were added in several portions. The reaction mixture was stirred for 30 min at room temperature. To the homogeneous mixture $HClO_4$ (70%, 0.5 mL) were added and the crude **2a** was precipitated with AcOMe (50 mL). This was filtered off, dried, and recrystallized from EtOH (100 mL) to give the pure product as colorless crystals; yield 0.43 g (70%).

Mp 161-162 °C. IR (ATR): 3579, 3114, 1560, 1528, 1440, 1253, 1065, 619 cm^{-1}. ^1H NMR (300 MHz, DMSO- d_6): δ = 1.41 (t, 6H, $2CH_3$), 4.02 (q, 4H, $2CH_2$), 6.52 (s, 1H, OH), 7.89 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 8.01 (s, 1H, H-5), 8.07 (d, ^4J = 2.4 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 518 (M^+- ClO_4).

4-(2-Hydroxy-3,5-diiodophenyl)-2-(3-methyl-piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**2e**):

Yield 76%. Mp 195-196 °C (dec). IR (ATR): 3570, 3125, 1574, 1523, 1410, 1258, 1070, 620 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 0.99 (d, 3H, CH_3-3), 1.31 (m, 1H, H-3), 1.88 (m, 4H, 2 H-4 + 2 H-5), 3.39 (m, 1H, H-2), 3.65 (m, 1H, H-2), 3.93 (m, 2H, H-6), 6.39 (s, 1H, OH), 7.95 (d, ^4J = 2.3 Hz, 1H, H_{ar}), 8.02 (s, 1H, H-5), 8.13 (d, ^4J = 2.4 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 544 (M^+-ClO_4).

4-(2-Hydroxy-3-iodo-5-methylphenyl)-5-ethyl-2-(3-methyl-piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**2h**):

Yield 70%. Mp 171-172 °C. IR (ATR): 3058, 1551, 1514, 1445, 1243, 1091, 1021, 619 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 0.98 (m, 3H, CH_3-3), 1.16 (t, 3H, CH_3), 1.24 (m, 1H, H-3), 1.90 (m, 4H, 2H-4 + 2H-5), 2.23 (s, 3H, CH_3-5), 2.58 (q, 2H, CH_2), 3.47 (m, 1H, H-2), 3.50 (m, 1H, H-6), 3.83 (m, 2H, H-2 + H-6), 6.88 (s, 1H, OH), 7.24 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 7.74 (d, ^4J = 2.4 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 460 (M^+-ClO_4).

4,6-Diiodo-2-[2-diethylamino-1,3-dithiol-2-ylium-4-yl]phenolate (**3a**)*; General Procedure*

To a saturated sodium hydrogencarbonate solution (30 mL) perchlorate **2a** (0.62 g, 1 mmol) 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 DMF gave yellow crystals; yield 0.51 g (99%).

Mp 222-223 °C (dec). IR (ATR): 3001, 1562, 1458, 1215, 780 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.40 (t, 6H, $2CH_3$), 4.01 (q, 4H, $2CH_2$), 6.5 (s, 1H, OH), 7.9 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 8.05 (s, 1H, H-5), 8.08 (d, ^4J = 2.4 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 517.

4,6-Diiodo-2-[2-(pyrrolidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**3b**):

Yield 100%. Mp 228-229 °C (dec). IR (ATR): 2987, 1561, 1510, 1472, 1409, 1218, 860, 788 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 2.28 (m, 4H, $2CH_2$), 3.78 (m, 4H, $2CH_2$), 7.89 (d, ^4J = 2.4 Hz, 1H, H_{ar}), 8.00 (s, 1H, H-5), 8.11 (d, ^4J = 2.4 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 515.

4,6-Diiodo-2-[2-(piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**3c**):

Yield 100%. Mp 210-211 °C (dec). IR (ATR): 1494, 1462, 1273, 849, 775, 618 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 1.67 (m, 2H, CH_2), 1.81 (m, 4H, $2CH_2$), 3.83 (m, 4H, $2CH_2$), 7.88 (d, ^4J = 2.3 Hz, 1H, H_{ar}), 8.02 (s, 1H, H-5), 8.12 (d, ^4J = 2.3 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 529.

4,6-Diiodo-2-[2-(morpholin-4-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**3d**):

Yield 100%. Mp 205-206 °C (dec). IR (ATR): 3001, 2968, 1547, 1495, 1470, 1448, 1342, 1221, 1195, 860, 788 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 3.92 (m, 8H, $4CH_2$), 6.32 (s, 1H, OH), 7.93 (d, ^4J = 2.3 Hz, 1H, H_{ar}), 8.02 (s, 1H, H-5), 8.13 (d, ^4J = 2.3 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 531.

4,6-Diiodo-2-[2-(3-methylpiperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**3e**):

Yield 100%. Mp 184-185 °C (dec). IR (ATR): 2860, 1459, 1255, 889, 791 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 0.98 (d, 3H, CH_3-3), 1.30 (m, 1H, H-3), 1.87 (m, 4H, 2 H-4 + 2 H-5), 3.39 (m, 1H, H-2), 3.63 (m, 1H, H-2), 3.93 (m, 2H, H-6), 7.94 (d, ^4J = 2.3 Hz, 1H, H_{ar}), 8.00 (s, 1H, H-5), 8.11 (d, ^4J = 2.3 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 543.

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

Yield 95%. Mp 204-205 °C (dec). IR (ATR): 2858, 1448, 1325, 1248, 888, 784 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 2.21 (m, 4H, $2CH_2$), 2.22 (s,

3H, CH_3-5), 3.68 (m, 4H, $2CH_2$), 7.52 (d, ^4J = 1.9 Hz, 1H, H_{ar}), 7.99 (d, ^4J = 1.9 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 529.

4,6-Diiodo-2-[5-methyl-2-(3-methylpiperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**3g**):

Yield 94%. Mp 192-193 °C (dec). IR (ATR): 2851, 1451, 1323, 1247, 884, 787 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 0.98 (m, 3H, CH_3-3), 1.24 (m, 1H, H-3), 1.91 (m, 4H, 2H-4 + 2H-5), 2.23 (s, 3H, CH_3-5), 3.48 (m, 1H, H-2), 3.51 (m, 1H, H-6), 3.84 (m, 2H, H-2 + H-6), 7.48 (d, ^4J = 2.0 Hz, 1H, H_{ar}), 8.01 (d, ^4J = 2.0 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 557.

6-Iodo-4-methyl-2-[5-ethyl-2-(3-methylpiperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**3h**):

Yield 100%. Mp 105-106 °C (dec). IR (ATR): 2848, 1447, 1320, 1245, 878, 783 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ = 0.96 (m, 3H, CH_3-3), 1.14 (t, 3H, CH_3), 1.23 (m, 1H, H-3), 1.89 (m, 4H, 2H-4 + 2H-5), 2.22 (s, 3H, CH_3-5), 2.57 (q, 2H, CH_2), 3.45 (m, 1H, H-2), 3.48 (m, 1H, H-6), 3.82 (m, 2H, H-2 + H-6), 7.21 (d, ^4J = 2.1 Hz, 1H, H_{ar}), 7.64 (d, ^4J = 2.1 Hz, 1H, H_{ar}). MS (ESI): *m/z* = 459.

References

1. Narita, M. and Pittmann Jr, C. U., Synthesis, **1976**, 489.
2. Laage, D., Thompson, W. H., Blanchard-Desce, M., and Hynes, J. T., *J. Phys. Chem. A*, **107**, 6032 (2003).
3. Fayed, T. A., *Colloids Surf* A, **236**, 171 (2004).

4. Yang, X., Liu, W. H., Jin, W. J., Shen, G. L., and Yu, R. Q., *Spectrochim. Acta, Part A*, **55**, 2719 (1999).
5. Bryce, M. R., *Adv. Mater.*, **11**, 11 (1999).
6. Goldenberg, L. M., Becker, J. Y., Levi, O. P. T., Khodorkovsky, V. Yu., Shapiro, L. M., Bryce, M. R., Cresswell, J. P., and Petty, M. C., *J. Mater. Chem.*, **7**, 901 (1997).
7. Simonsen, K. B., Zong, K., Rogers, R. D., Cava, M. P., and Becher, J., *J. Org. Chem*. **62**, 679 (1997).
8. Masternak, A., Wenska, G., Milecki, J., Skalski, B., and Franzen, S., *J. Phys. Chem. A,* **109**, 759 (2005).
9. Birsa, M. L., *Synth. Commun.,* **31**, 1271 (2001).
10. Ueno, Y., Nakayama, A., and Okawara, M., *Synthesis* 277 (1975).
11. Birsa, M. L., *An. St. Univ. Al. I. Cuza Iasi, s. Chimie,* **6**, 57 (1998).
12. Birsa, M. L., *Sulfur Lett.,* **26**, 155 (2003).
13. Birsa, M. L., *An. St. Univ. Al. I. Cuza Iasi, s. Chimie,* **7**, 341 (1999).
14. Miller, J., Oliveira, M. B., Pereira, A. B., Galembeck, S. E., Moura, G. L. C., and Simas, A. M., *Phosphorus Sulfur Silicon Relat. Elem.*, **108**, 75 (1996).
15. Simas, A. M., Miller, J., and Athayde Filho, P. F., *Can. J. Chem.*, **76**, 869 (1998).
16. Athayde Filho, P. F., Miller, J., and Simas, A. M., *Synthesis*, **2000**, 1565.