Mesoionic 4-(2-Dialkylamino-1,3-dithiol-2-ylium-4-yl)phenolates

PAUL CHIRITA[1], IULIEAN VASILE ASAFTEI[2], ION SANDU[3], LAURA GABRIELA SARBU[2], VASILE VALERIU LUPU[4]*

[1] University of Craiova, Department of Chemistry, 107I Calea Bucuresti, 200478, Craiova, Romania

[2] Al. I. Cuza University of Iasi, Department of Chemistry, 11 Carol I Blvd., 700506, Iasi, Romania

[3] Alexandru Ioan Cuza University of Iasi, ARHEOINVEST Interdisciplinary Platform, 22 Carol I Blvd., 700506, Iasi, Romania

[4] Grigore T. Popa University of Medicine and Pharmacy Iasi, Mother and Child Department, 16 Universitatii Str., 700115, Iasi, Romania

New mesoionic 4-(2-dialkylamino-1,3-dithiol-2-ylium-4-yl)phenolates have been obtained from the corresponding 1,3-dithiolium salts under weak basic conditions. The 1,3-dithiolium salts have been synthesized by the cyclocondensation of 1-(4-hydroxyphenyl)-1-oxaethan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the 2-bromo-1-(4-hydroxyphenyl)ethan-1-one with various salts of dithiocarbamic acids. UV-Vis investigations proved the intramolecular charge transfer for the mesoionic 1,3-dithiolium phenolates.

Keywords: hydroxyacetophenones, dithiocarbamates, 1,3-dithiolium salts, mesoionic compounds, UV-Vis spectroscopy

Heterocycles represent a unique class of compounds that exhibit a large range of applications [1-3]. Along with a wide variety of the applications in material chemistry, heterocyclic compounds also exhibit strong implication in therapeutics [4-10]. A special interest has attracted the nitrogen or/and sulfur containing heterocyclic compounds [11-28]. Among these compounds 1,3-dithiolium derivatives have received a particular interest, especially due to their reactivity at the C(2)-position towards nucleophiles [29,30]. Furthermore, 1,3-dithiolium salts are also important precursors in the synthesis of tetrathiafulvalenes, that are used as good π-electron donors in obtaining organic metals. Recent studies highlighted the role of tetrathiafulvalenes as donor groups in intramolecular charge-transfer complexes [31]. In this context, a variety of acceptor units has been investigated, special attention being devoted to the nature of cationic systems. Thus, particular attention has been paid to the systems where the donor moiety is linked through a π- or σ-bonded bridge to the acceptor moiety [32-44]. Recently, new evidences for the mesoionic character of 2-(1,3-dithiol-2-ylium)phenolates (*lasinones*) have reported reported [45, 46]. These data have been obtained from bromination reactions of the 1,3-dithiolium ring. Prompted by these previous findings we report here the synthesis of a new series of mesoionic 4-(2-dialkylamino-1,3-dithiol-2-ylium-4-yl)phenolates. These compounds are also of biological interest; their biological activity will be investigated in the future.

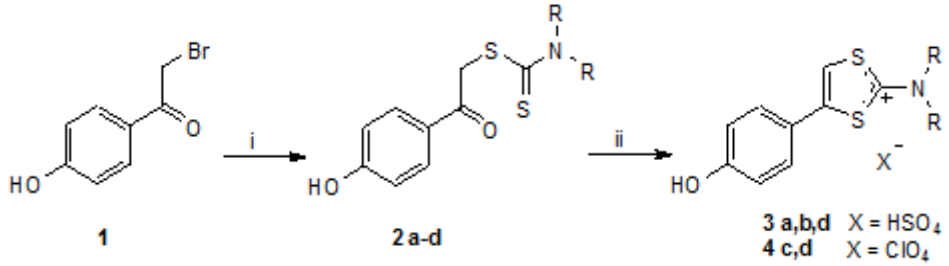
Experimental part

Analysis methods

Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. UV-Vis spectra were recorded on a Varian BioCarry 100 Spectrophotometer. NMR spectra were recorded on a Bruker DPX-300 Spectrometer. Chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N and S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.31%) with the calculated values.

Synthesis

The synthetic pathway for the synthesis of carbodithioates **2a, b** and 1,3-dithiolium derivatives **3a, b** is described in scheme 1.



1 **2 a-d** **3 a,b,d** X = HSO_4 **4 c,d** X = ClO_4

i. $R_2NC(S)S^-$, acetone, reflux; ii. H_2SO_4/AcOH 1:3 (v/v), 80 °C

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

Scheme 1. Synthesis of dithiocarbamates **2** and 1,3-dithiolium salts **3** and **4**

* *email: valeriulupu@yahoo.com*

Table 1
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM HYDROGEN SULPHATES **3**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
3a	240-241 dec.	90	3256, 1661, 1601, 1564, 1448, 1320, 1218, 1099, 958, 832	*^1H NMR* δ : 3.48 (3H, s, CH_3), 3.75 (3H, s, CH_3), 5.88 (2H, s, OH + HSO_4), 6.82 (1H, d, H-2), 7.40 (1H, d, H-6; ^3J=7.4 Hz), 7.66 (1H, s, H-5). *^{13}C NMR* δ : 47.5, 47.8, 115.4, 116.5, 121.2, 128.9, 139.4, 159.7, 186.1 .
3b	223-224	84	3268, 1675, 1609, 1578, 1458, 1327, 1223, 1095, 960, 840	*^1H NMR* δ : 1.38 (6H, t, $2CH_3$), 3.88 (2H, q, CH_2), 3.92 (2H, q, CH_2), 5.53 (2H, s, OH + HSO_4), 6.89 (1H, d, H-2), 7.45 (1H, d, H-6, ^3J=7.4 Hz), 7.80 (1H, s, H-5). *^{13}C NMR* δ : 17.7, 53.7, 54.4, 115.3, 116.8, 121.0, 129.1, 139.3, 159.9, 186.0 .
3d	244-245 dec.	88	3215, 1648, 1590, 1450, 1314, 1246, 1205, 1101, 1025, 986	*^1H NMR* δ : 3.92 (8H, m, $4CH_2$), 6.00 (2H, s, OH + HSO_4), 6.94 (1H, d, H-2), 7.52 (1H, d, H-6, ^3J=7.5 Hz), 7.85 (1H, s, H-5). *^{13}C NMR* δ : 54.0, 54.5, 64.4, 115.1, 116.4, 120.9, 128.8, 139.2, 159.7, 186.2 .

1-(4-Hydroxyphenyl)-1-oxaethan-2-yl-morpholine-4-carbodithioate (**2d**)

To a solution of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (**1**, 2.15 g, 10 mmol) in acetone (50 mL), a solution of morpholinium morpholine-4-carbodithioate (2.5g, 10 mmol) in acetone-water (1:1, 80 mL) was added. The reaction mixture was refluxed for 10 min, cooled to room temperature and then poured into water. The precipitate was filtered, washed with water and dried off. Recrystallization from ethanol (80 mL) gave colorless crystals; yield 2.53g (85%). M.p. = 211-212°C. IR(ATR): 3210, 2924, 1658, 1572, 1411, 1270, 1159, 981, 821, 610 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.74 (4H, m, CH_2-O-CH_2), 4.13 (4H, m, CH_2-N-CH_2), 4.81 (2H, s, CH_2), 6.85 (2H, d, H-2+H-6); 7.90 (2H, d, H-3+H-5; ^3J=8.1 Hz), 9.95 (1H, s, OH) ppm. ^{13}C NMR ($CDCl_3$) δ : 43.8, 51.3, 52.0, 66.0, 115.0, 127.9, 130.6, 161.6, 191.1, 193.5 ppm.

4-(4-Hydroxyphenyl)-2-(morpholin-4-yl)-1,3-dithiol-2-ylium hydrogen sulphate (**3d**); *General Procedure*

To a mixture of sulfuric acid (98%, 2 mL) and glacial acetic acid (6 mL), 1-(4-hydroxyphenyl)-1-oxaethan-2-yl-morpholine-4-carbodithioate (**2d**, 2 g, 6.7 mmol) was added in small portions. The reaction mixture was heated at 80°C for 10 min. The reaction mixture that solidified on cooling was washed with ether, filtered and dried off. Recrystallization from aqueous sulfuric acid (1N, 100 mL) gave colorless crystals; yield 2.23g (88%). Analytical and spectral data of 1,3-dithiolium hydrogen sulphates **3** are presented in table 1.

4-(4-Hydroxyphenyl)-2-(piperidin-1-yl)-1,3-dithiol-2-ylium perchlorate (**4c**); *General Procedure*

To a mixture of sulfuric acid (98%, 1 mL) and glacial acetic acid (3 mL), 1-(4-hydroxyphenyl)-1-oxaethan-2-yl-morpholine-4-carbodithioate (**2c**, 1 g, 3.3 mmol) was added in small portions. The reaction mixture was heated at 80°C for 10 min and then $HClO_4$ (70%, 0.5 mL) was added. After cooling, methyl acetate (100 mL) was added and the precipitate was filtered and dried off. Recrystallization from ethanol (50 mL) gave colorless crystals; yield 1.11g (87%). Analytical and spectral data of 1,3-dithiolium hydrogen sulphates **4** are presented in table 2.

4-[2-(Piperidin-1-yl)-1,3-dithiol-2-ylium-4-yl]phenolate (**5c**)*; General Procedure*

To a saturated sodium hydrogen carbonate solution (20 mL), 1,3-dithiolium perchlorate **4c** (1 g, 2.6 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 ethanol gave yellow crystals; yield 0.73 g (100%). Analytical and spectral data of 1,3-dithiolium phenolates **5** are presented in table 3.

Results and discussions

The synthesis of 4-(4-hydroxyphenyl)-2-(*N,N*-dialkylamino)-1,3-dithiolium salts can be easily accomplished by the cyclization of the corresponding *N,N*-dialkylamino carbodithioates. The latter compounds are easily available from 4-hydroxyacetophenone, following a two step synthetic procedure. The synthesis of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (**1**) has been accomplished by the selective monobromination of the side chain. This reaction has been performed using the molecular complex of bromine with dioxane [47]. Although this reagent has been often employed in mild and selective bromination reactions [48], there are some difficulties on isolation and handling of this compound [49]. In order to avoid these problems we performed the selective side chain bromination of 4-hydroxyacetophenone using *in situ* obtained molecular complex of bromine with dioxane. Thus, one equivalent of bromine was mixed with one

Table 2
ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOLIUM PERCHLORATES **4**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
4c	196-197 dec.	87	3244, 1604, 1570, 1501, 1434, 1257, 1110, 830	*^1H NMR* δ : 1.77 (6H, m, $3CH_2$), 3.87 (4H, m, $2CH_2$-N), 6.91 (1H, d, H-2), 7.48 (1H, d, H-6; ^3J =7.0 Hz), 7.67 (1H, s, H-5), 10.18 (1H, s, OH). *^{13}C NMR* δ : 21.5, 24.8, 25.0, 56.5, 57.6, 115.3, 116.7, 121.2, 128.9, 139.4, 159.9, 186.1 .
4d	247-248 dec.	81	3186, 1599, 1568, 1514, 1438, 1247, 1095, 821	*^1H NMR* δ : 3.92 (8H, m, $4CH_2$), 6.93 (1H, d, H-2), 7.49 (1H, d, H-6, ^3J =7.2 Hz), 7.75 (1H, s, H-5), 10.20 (1H, s, OH). *^{13}C NMR* δ : 53.8, 54.2, 64.3, 115.1, 116.5, 121.0, 128.7, 139.6, 160.3, 186.0 .

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

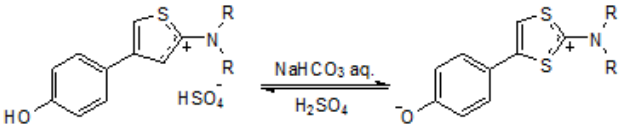
	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR (DMSO-*d6*), ppm
5a	120-121 dec.	100	3112, 1561, 1391, 1324, 1248, 847, 815, 775	*^1H NMR* δ : 3.58 (6H, s, $2CH_3$), 6.95 (1H, d, H-2); 7.51 (1H, d, H-6; ^3J =7.0 Hz); 7.77 (1H, s, H-5). *^{13}C NMR* δ : 47.4, 47.8, 115.3, 116.5, 121.1, 128.7, 139.5, 159.7, 186.0 .
5b	97-98 dec.	100	3115, 1568, 1395, 1325, 1241, 841, 805, 780	*^1H NMR* δ : 1.36 (6H, t, $2CH_3$), 3.82 (2H, q, CH_2), 3.87 (2H, q, CH_2), 6.91 (1H, d, H-2), 7.51 (1H, d, H-6; ^3J=7.1 Hz), 7.74 (1H, s, H-5). *^{13}C NMR* δ : 17.5, 53.6, 54.5, 115.4, 116.7, 121.0, 129.0, 139.3, 159.7, 186.1 .
5c	212-213 dec.	100	3071, 1574, 1444, 1249, 829, 750	*^1H NMR* δ : 1.79 (6H, m, $3CH_2$), 3.81 (4H, m, $2CH_2$-N), 6.94 (1H, d, H-2); 7.51 (1H, d, H-6; ^3J=7.1 Hz), 7.73 (1H, s, H-5). *^{13}C NMR* δ : 21.3, 24.7, 25.1, 56.4, 57.6, 115.1, 116.5, 121.2, 128.9, 139.5, 159.7, 186.3 .
5d	200-201 dec.	100	2901, 1570, 1438, 1398, 1245, 1178, 850, 820	*^1H NMR* δ : 3.48 (8H, m, $4CH_2$), 6.88 (1H, d, H-2); 7.65 (1H, d, H-6; ^3J =7.1 Hz), 7,68 (1H, s, H-5). *^{13}C NMR* δ : 53.7, 54.1, 64.4, 115.3, 116.3, 121.2, 128.8, 139.9, 160.1, 186.1 .

equivalent of dioxane and to the resulting solid dry dioxane was added until complete dissolution. This solution was added dropwise at room temperature to a solution of one equivalent of 4-hydroxyacetophenone in dioxane.

The treatment of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (**1**) with various salts of dialkyldithiocarbamic acid, compounds that are readily available from the reaction of secondary amine with carbon disulfide [50], provided *N,N*-dialkylamino carbodithioates **2**. While the synthesis of phenacylcarboditioates **2a-c** has been previously reported [32], 1-(4-hydroxyphenyl)-1-oxaethan-2-yl-morpholine-4-carbodithioate (**2d**) has been synthesized from the reaction of 2-bromo-1-(4-hydroxyphenyl)ethan-1-one (**1**) with morpholinium morpholine-4-carbodithioate. The structure of dithiocarbamate **2d** has been proved by analytical and spectral data. The ^{1}H NMR spectra indicate the signals corresponding to the methylene groups in morpholine moiety (3.74 and 4.13 ppm). ^{13}C NMR spectra indicate the appearance of additional signals above the 190ppm, attributed to the thiocarbonyl group.

Using a concentrated sulfuric acid-glacial acetic acid (1:3 v/v) mixture [51-60] the cyclization of dithiocarbamates **2a-d** takes place under mild reaction conditions (scheme 1). After 10 min at 80°C the 1,3-dithiolium salts have been obtained as hydrogen sulphates **3** or perchlorates **4**, depending on the experimental procedure. These compounds have been obtained as colorless crystals, in good to excellent yields (table 1 and 2). The cyclization of dithiocarbamates **2** was accompanied by important spectral changes. The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (ca. 1650 cm^{-1}) and the presence of new, strong and broad absorption bands at ca. 1100 cm^{-1}, corresponding to the hydrogen sulphate or perchlorate anions. Heterocyclization of dithiocarbamates **2** is also supported by the NMR spectra. Thus, the ^{1}H NMR spectra of 1,3-dithiol-2-ylium hydrogen sulphates indicate the absence of the *a*-carbonyl hydrogens from compounds **2** (ca. 4.8 ppm). ^{13}C NMR spectra also support the synthesis of 1,3-dithiolium salts **3** and **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 (186ppm) which correspond to the electron deficient C(2) atom.

Treatment of hydrogen sulphates **3**, under heterogeneous conditions, with saturated aqueous sodium hydrogen carbonate solution provides 4-[2-(*N,N*-dialkylamino)-1,3-dithiol-2-ylium-4-yl]phenolates **5** in quantitative yields as yellow compounds (scheme 2). The molecular structure of the new compounds was proved by analytical and spectral data (table 3) and by the following chemical transformation: treatment of an acetone



3 **5**

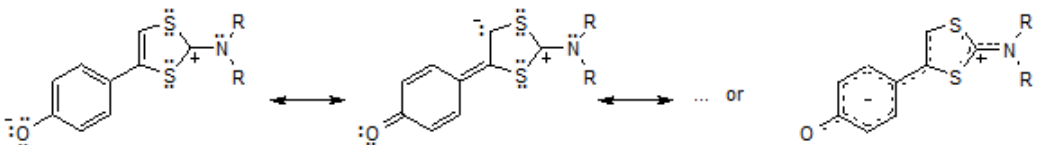
Scheme 2. Synthesis of mesoionic phenolates **5** and their interconversion with the corresponding 1,3-dithiolium hydrogen sulphates **3**

suspension of the mesoionic compounds **4** with sulfuric acid regenerates the 1,3-dithiolium hydrogen sulphates **3** in quantitative yields (scheme 2).

As mentioned before, phenolates **4** have been isolated as yellow products that present the features of mesoionic compounds [61]. The presence of a hydroxy substituent in the *para*-position induces an extended delocalization of the negative charge up to the C(4)-C(5) bond of the dithiolium ring (scheme 3).

In a previous paper [32], 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 the above 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. The intramolecular nature of the charge-transfer band was proved by measurements at different concentrations. Investigations of UV-Vis absorption spectra of mesoionic phenolates **5** confirm the previous findings (fig. 1).

While the intramolecular charge-transfer UV-Vis absorption of such chromophores results from a charge transfer from the HOMO of the donor part to the LUMO of the acceptor part, the electronic effects of the substituents on the extended delocalization of the negative charge should result on a HOMO orbital of lower energy. Thus, the presence of phenolic substituent at the *para* position to the 1,3-dithiolium ring results in an extended conjugation that



Scheme 3. Extended delocalization charge in mesoionic phenolates **5**

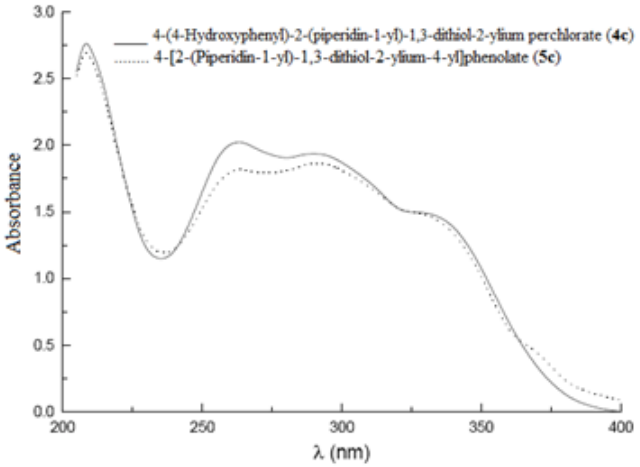


Fig. 1. UV/Vis absorption spectra of 1,3-dithiolium perchlorate **4c** and mesoionic phenolate **5c** in methanol

prompted an enhancement of all absorption bands and the appearance of a new absorption band at 290 nm. The charge transfer absorption band of mesoionic phenolates **5** (370 nm) is overlapped by the large absorption band centered at 335 nm. As a result of the extended conjugation, the spectrum of mesoionic phenolate **5c** indicates a new absorption band at 295 nm that belongs to the contribution of the *para*-quinoid structure to the real state of the molecule (scheme 3).

Conclusions

New mesoionic 4-(2-dialkylamino-1,3-dithiol-2-ylium-4-yl)phenolates have been synthesized by the hetero-condensation of the 1-(4-hydroxyphenyl)-1-oxaethan-2-yl dithiocarbamates. The latter compounds have been obtained from the reaction of the corresponding substituted 2-bromo-1-(4-hydroxyphenyl)ethan-1-one with various salts of dithiocarbamic acids. UV-Vis investigations proved the intramolecular charge transfer for the mesoionic 1,3-dithiolium phenolates **5** and also revealed a *para*-quinoid structure for these compounds.

Acknowledgments: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNDI– UEFISCDI, project number 51/2012.

References

1. NEKRASOV, D.D., Chemistry of Heterocyclic Compounds, **37**, 2001, p. 263.
2.NORMAN, S.R., Drug Development Res., **69**, 2008, p. 15.
3.DUA, R., SHRIVASTAVA, S., SONWANE, S.K., SRIVASTAVA, S.K., Adv. Biolog. Res., **5**, 2008, p. 120.
4.GOSAV, S., BIRSA, M.L., Acta Chem. Iasi, **18**, 2010, p. 150.
5.SARBU, L.G., BIRSA, A., HOPF, H., BIRSA, M.L., Phosphorus, Sulfur, and Silicon, and the Related Elements, **186**, 2011, p. 1246.
6.BELEI, D., BICU, E., JONES, P. G., BIRSA, M.L., J. Heterocycl. Chem., **48**, 2011, p. 129.
7.GOSAV, S., PRAISLER, M., BIRSA, M.L., Int. J. Mol. Sci., **12**, 2011, p. 6668.
8.BELEI, D., ABUHAIE, C., BICU, E., JONES, P. G., HOPF, H., BIRSA, M.L., Synlett, **23**, 2012, p. 545.
9.BAHRIN, L.G., APOSTU, M.O., BIRSA, M.L., STEFAN, M., Bioorg. Med. Chem. Lett., **24**, 2014, p. 2315.
10.GOSAV, S., BIRSA, M.L., Rom. Rep. Phys., **66**, 2014, p. 411.
11.SELIGER, H., HAPP, E., CASCAVAL, A., BIRSA, M.L., An. Stiint. Univ. Al.I. Cuza Iasi, **5**, 1997, p. 111.
12.SELIGER, H., CASCAVAL, A., BIRSA, M.L., An. Stiint. Univ. Al.I. Cuza Iasi, **5**, 1997, p. 129.
13.BIRSA, M.L., An. Stiint. Univ. Al.I. Cuza Iasi, **8**, 2000, p. 325.
14.BRAVERMAN, S., CHERKINSKY, M., BIRSA, M.L., TICHMAN, S., GOLDBERG, I., Tetrahedron Lett., **42**, 2001, p. 7485.
15.BIRSA, M.L., CHERKINSKY, M., BRAVERMAN, S., Tetrahedron Lett., **43**, 2002, p. 9615.
16.BIRSA, M. L., Synth. Commun., **32**, 2002, p. 115.
17.BELEI, D., BICU, E., BIRSA, M.L., Acta Chem. Iasi, **17**, 2009, p. 197.
18.BELEI, D., BICU, E., JONES, P. G., BIRSA, M. L., Synlett, **2010**, p. 931.
19.BAHRIN, L.G., JONES, P.G., HOPF, H., Beilstein J. Org. Chem., **8**, 2012, p. 1999.
20.MARIN, L., ARVINTE, A., Mat. Plast., **50**, no. 1, 2013, p. 23.
21.SARAVANAKUMARA, R., MARKOPOULOS, G., BAHRIN, L.G., HOPF, H., Synlett, **24**, 2013, p. 453.
22.BAHRIN, L.G., LUNGU, N.C., FORNA, N.C., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **64**, no. 11, 2013, p. 1343.
23.SARBU, L.G., BICU, E., HOPF, H., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 4, 2014, p. 398.
24.BAHRIN, L.G., LUCA, A., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 199.
25. BIRSA, M.L., SANDU, I., BAHRIN, L.G., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 174.
26.SARBU, L.G., HOPF, H., GRUENENBERG, J., BIRSA, M.L., Synlett, **26**, 2015, p. 87.
27.SARBU, L.G., HOPF, H., JONES, P.G., BIRSA, M.L., Beilstein J. Org. Chem., **10**, 2014, p. 2550.
28.SARBU, L.G., LUNGU, N.C., BALAN, A., BAHRIN, L.G., Rev. Chim. (Bucharest), **65**, no. 10, 2014, p. 1135.
29.BIRSA, M.L., Synth. Commun., **33**, 2003, p. 3071.
30.BAHRIN, L.G., CRACIUN, B.F., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 5, 2014, p. 525.
31.BRYCE, M.R., GREEN, A., MOORE, A.J., PEREPICHKA, D.F., BATSANOV, A.S., HOWARD, J.A.K., LEDOUX-RAK, I., GONZALES, M., MARTIN, N., SEGURA, J.L., GARIN, J., ORDUNA, J., ALCALA, R., VILLACAMPA, B., Eur. J. Org. Chem., **2001**, p. 1927.
32. BIRSA, M.L., GANJU, D., J. Phys. Org. Chem., **16**, 2003, p. 207.
33.BIRSA, M.L., JONES, P.G., BRAVERMAN, S., HOPF, H., Synlett, **2005**, p. 640.
34.BIRSA, M.L., HOPF, H., Synlett, **2007**, p. 2753.
35.BIRSA, M.L., ASAFTEI, I.V., Monat. Chem., **139**, 2008, p. 1433.
36.BIRSA, M.L., HOPF, H., Synlett, **2009**, p. 3000.
37.BIRSA, M.L., HOPF, H., Heteroatom Chem., **21**, 2010, p. 126.
38.BIRSA, M.L., JONES, P.G., HOPF, H., Synlett, **2011**, p. 259.
39.LUNGU, N.C., SANDU, I., CHIRITA, P., BIRSA, M.L., Rev. Chim. (Bucharest), **64**, no. 7, 2013, p. 697.
40.SARBU, L.G., BAHRIN, L.G., Acta Chem. Iasi, **21**, 2013, p. 47.
41.LUNGU, N.C., BAHRIN, L.G., ASAFTEI, I.V., FORNA, N.C., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 181.
42.SARBU, L.G., APOSTU, M.O., SANDU, I.G., MANEA, L.R., BAHRIN, L.G., Rev. Chim. (Bucharest), **65**, no. 11, 2014, p. 1327.
43.BAHRIN, L.G., ASAFTEI, I.V., SANDU, I.G., SARBU, L.G., Rev. Chim. (Bucharest), **65**, no. 9, 2014, p. 1046.
44.HOPF, H., JONES, P.G., NICOLESCU, A., BICU, E., BIRSA, M.L., BELEI, D., Chem. Eur. J., **20**, 2014, p. 5565.
45.SARBU, L.G., LUNGU, C.N., ASAFTEI, I.V., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 3, 2014, p. 325.
46.SARBU, L.G., SANDU, I., BAHRIN, L.G., BALAN, A., APOSTU, M.O., Rev. Chim. (Bucharest), **66**, no. 1, 2015, p. 55.
47.PASARIBU, S.J., WILLIAMS, L.R., Aust. J. Chem., **26**, 1973, p. 1327.
48.DOMBROVSKI, A.V., Russ. Chem. Revs., **30**, 1961, p. 635.
49.BILLIMORIA, J.D., Maclagen, N.F., J. Chem. Soc., **1954**, p. 3257.
50.BRAVERMAN, S., CHERKINSKY, M., BIRSA, M.L., Science of Synthesis, **18.2**, Georg Thieme Verlag, Stuttgart, 2005, p 55.
51.BIRSA, M.L., An. St. Univ. Al. I. Cuza Iasi, s. Chimie, **6**, 1998, p. 57.
52.BIRSA, M.L., An. St. Univ. Al. I. Cuza Iasi, s. Chimie, **7**, 1999, p. 341.
53.BIRSA, M.L., An. St. Univ. Al. I. Cuza Iasi, s. Chimie, **7**, 1999, p. 349.
54.SELIGER, H., HAPP, E., CASCAVAL, A., BIRSA, M.L., NICOLAESCU, T., POINESCU, I., COJOCARIU, C., Eur. Polym. J., **35**, 1999, p. 827.
55.BIRSA, M.L., An. St. Univ. Al. I. Cuza Iasi, s. Chimie, **8**, 2000, p. 71.
56.BIRSA, M.L., An. St. Univ. Al. I. Cuza Iasi, s. Chimie, **8**, 2000, p. 329.
57. BIRSA, M.L., Synth. Commun., **31**, 2001, p. 1271.
58.BIRSA, M.L., Sulfur Lett., **26**, 2003, p. 155.
59.SARBU, L.G., BIRSA, M.L., Acta Chem. Iasi, **19**, 2011, p. 125.
60.BELEI, D., FORNA, N.C., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 1, 2014, p. 80.
61.ATHAYDE FILHO, P.F., MILLER, J., SIMAS, A.M., Synthesis- Stuttgart, **11**, 2000, p. 1565.

Manuscript received: 3.07.2016