New 4-(4-Hydroxyaryl)-5-Methyl-1,3-Dithiol-2-ylidene Derivatives

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New 4-(3,5-dibromo-4-hydroxyphenyl)-5-methyl-1,3-dithiol-2-ylidene derivatives have been synthesized from the reaction of the corresponding 4-(4-hydroxyaryl)-2-N,N-dimethylamino-1,3-dithiol-2-ylium perchlorate with various methylene active compounds under basic conditions. The 1,3-dithiol-2-ylium compounds have been obtained from the reaction of the substituted α-bromo-4-hydroxypropiophenone with sodium N,N-dimethyldithiocarbamate.

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

The development of new organic superconductors still remains a major topic in the field of molecular conductors [1]. Since the discovery of the metallic conductivity in a tetrathiafulvalene-tetracyanoquinodimethane complex [2] and the subsequent discovery of the first organic superconductor, a tetramethyltetraselenafulvalene derivative [3], tetrachalcogenafulvalenes have played a leading role in the development of new molecular metals and superconductors [4, 5]. For many years, all the organic π-electron donors with conductivity properties were limited to the tetrachalcogenafulvalenes compounds [6, 7]. Recently, the non-tetrachalcogenafulvalenes containing a 1,3-dithiol-2-ylidene based π-donor unity proved to give superconducting salts [8]. Moreover, novel dye-sensitized solar cells based on 1,3-dithiol-2-ylidene derivatives have been recently reported [9]. For these reasons heterocyclic compounds - especially those containing sulfur - represent an important resource for the material chemistry and not only [10-25]. An important precursor for 1,3-dithiol-2-ylidene derivatives are the 1,3-dithiolium-2-yl compounds. These systems contain a positive charge located at the C(2) position and for this reason these systems are well known for the reactivity towards nucleophiles [26]. 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 [27].

We are reporting here the synthesis of new 4-(3,5-dibromo-4-hydroxyphenyl)-5-methyl-1,3-dithiol-2-ylidene derivatives from the corresponding 1,3-dithiolium salts by the nucleophilic attack of methylene active compounds at the C(2) position of the 1,3-dithiolium ring. These compounds might also be of biological interest since the 1,3-dithiolium ring is known to exhibit such properties. Thus, the biological activities will be investigated in the future.

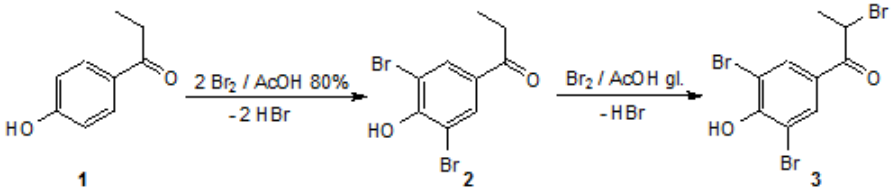
Experimental part

Analysis methods

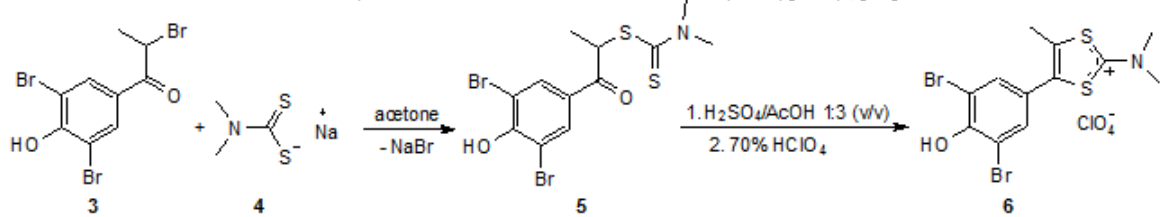
Melting points were obtained on a Mel-Temp II apparatus. IR spectra were recorded on a Bruker Tensor 27 instrument. NMR spectra were recorded on a Bruker DPX-300 Spectrometer. Chemical shifts are reported in ppm downfield from TMS. Elemental analyses (C, H, N and S) were conducted using a CE440 Elemental Analyser; the results were found to be in good agreement (±0.35%) with the calculated values.\

Synthesis

The reaction sequence for the synthesis of dithiocarbamate **5**, 1,3-dithiolium perchlorate **6** and of their precursors is described in Scheme 1 and 2. 1,3-Dithiol-2-ylidene derivatives **9a-d** were accomplished using the reaction pathway presented in scheme 3.



Scheme 1. Synthesis of 2-bromo-1-(3,5-dibromo-4 hydroxyphenyl)propan-1-one



Scheme 2. Synthesis of dithiocarbamate **5** and 1,3-dithiolium perchlorate **6**

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1-(3,5-Dibromo-4-hydroxyphenyl)-1-oxapropan-2-yl-N,N-dimethyldithiocarbamate (**5**)

To a solution of 2-bromo-1-(3,5-dibromo-4-hydroxyphenyl)propan-1-one (**3**, 1.16 g, 3 mmol) in acetone (50 mL), a solution of sodium *N,N*-dimethyldithiocarbamate hexahydrate (**4**, 0.76g, 3mmol) in acetone-water (1:1, 10 mL) 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 (25 mL) gave colorless crystals; yield 1.0 g (80%). M.p. = 145-146°C. IR (ATR): 3350, 1678, 1576, 1377, 1296, 1240, 1133, 960, 726, 633 cm^{-1}. ^1H NMR ($CDCl_3$) δ : 1.58 (3H, d, CH_3); 3.38 (2H, t, N-CH_2); 3.56 (2H, t, N-CH_2); 5.68 (1H, q, ^3J = 7.1 Hz) CH); 6.41 (1H, s, OH); 8.24 (2H, s, H-4+H-6) ppm. ^{13}C NMR ($CDCl_3$) d : 16.8, 41.7, 45.9, 51.6, 110.1, 130.1, 133.0, 153.4, 193.4, 194.3 ppm.

4-(3,5-Dibromo-4-hydroxyphenyl)-5-methyl-2-N,N-dimethylamino-1,3-dithiol-2-ylium perchlorate (**6**)

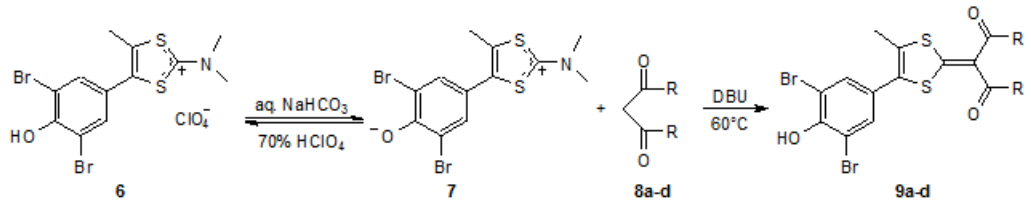
To a mixture of sulfuric acid (98%, 1mL) and glacial acetic acid (3 mL), 1-(3,5-dibromo-4-hydroxyphenyl)-1-oxapropan-2-yl-*N,N*-dimethyldithiocarbamate (**5**, 1 g, 2.34 mmol) was added in small portions. The reaction mixture was heated at 80°C for 10 min. After cooling, 70% $HClO_4$ (0.5 mL) and then water (100 mL) were added and the precipitate was filtered and dried off. Recrystallization from ethanol (500 mL) gave colorless crystals; yield 1.04 g (87%). M.p. = 261-262°C dec. IR(ATR): 3320, 1560, 1474, 1105, 1049, 879, 740, 621 cm^{-1}. ^1H NMR (DMSO-*d*6) δ : 2.38 (3H, s, CH_3-5); 3.51 (3H, s, N-CH_3); 3.52 (3H, s, N-CH_3); 7.75 (2H, s, H-4+H-6); 10.69 (1H, s, OH) ppm. ^{13}C NMR (DMSO-*d*6) δ : 15.1, 47.3, 47.5, 112.7, 122.8, 129.4, 132.1, 133.5, 152.9, 183.9 ppm.

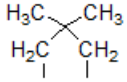
2,6-Dibromo-4-[5-methyl-2-N,N-dimethylamino-1,3-dithiol-2-ylium-4-yl]phenolate (**7**)

To a saturated sodium hydrogen carbonate solution (15mL), perchlorate **6** (1.02 g, 2 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 0.82 g (100%). M.p.=186-187°C dec. IR(ATR): 3360, 1572, 1438, 1407, 1233, 865, 719, 629 cm^{-1}. ^1H NMR (DMSO-*d*6) δ : 2.38 (3H, s, CH_3-5); 3.52 (6H, s, N-CH_3); 7.74 (2H, s, H-4+H-6) ppm. ^{13}C NMR (DMSO-*d*6) δ : 15.0, 47.2, 47.5, 112.8, 122.7, 129.4, 132.0, 133.5, 153.1, 184.0 ppm.

1,3-Dithiol-2-ylidene derivative **9b**; *General Procedure*

To a solution of mesoionic phenolate **7** (0.41 g, 1 mmol) in acetonitrile (15 mL) under nitrogen atmosphere, dimethylmalonate (**8b**, 0.16 mL, 1.05 mmol) and DBU (0.17 mL, 1.1 mmol) was added and the reaction mixture was brought to 60°C. The reaction was left over night under stirring. The solution was then poured into water (100 mL)



8, 9	R	R'
a	CH_3	CH_3
b	OMe	OMe
c		
d		

Scheme 3. Synthesis of 1,3-dithiol-2-ylidene derivatives ***9a-d***

Table 1

ANALYTICAL AND SPECTRAL DATA OF 1,3-DITHIOL-2-YLIDENE DERIVATIVES **9a-d**

	M.p., °C	η, %	IR-ATR, cm^{-1}	NMR, ppm
9a	223-224	96	1637, 1571, 1469, 1362, 1318, 717, 613, 506	*^1H NMR* ($CDCl_3$) δ : 2.28 (3H, s, CH_3); 2.58 (6H, bs, $2CH_3$); 6.08 (1H, bs, OH); 7.61 (2H, s, H-2+H-6). *^{13}C NMR* ($CDCl_3$) δ : 14.0, 30.8, 30.9, 101.4, 112.8, 125.0, 130.8, 132.3, 133.2, 152.6, 173.4, 191.5, 191.6 .
9b	269-270	69	3378, 1631, 1399, 1282, 1020, 790, 743, 501	*^1H NMR* (DMSO-*d*6) δ : 2.27 (3H, s, CH_3); 3.74 (3H, s, CH_3); 3.75 (3H, s, CH_3); 7.66 (2H, s, H-2+H-6); 10.46 (1H, bs, OH). *^{13}C NMR* (DMSO-*d*6) δ : 14.0, 52.3, 52.4, 101.0, 112.7, 124.8, 130.6, 132.5, 133.1, 152.1, 165.9, 166.0, 175.7 .
9c	197-198	89	1573, 1473, 1375, 739, 566, 513	*^1H NMR* ($CDCl_3$) δ : 1.10 (6H, s, 2 CH_3); 2.43 (3H, s, CH_3); 2.57 (2H, s, CH_2); 2.58 (2H, s, CH_2); 4.35 (1H, bs, OH); 7.55 (2H, s, H-2+H-6). *^{13}C NMR* ($CDCl_3$) δ : 14.0, 28.5, 30.9, 50.6, 50.7, 110.8, 117.0, 124.9, 132.8, 133.6, 133.8, 151.0, 173.3, 193.13, 193.15 .
9d	271-272	78	1647, 1587, 1447, 1335, 1205, 730, 652, 524	*^1H NMR* (DMSO-*d*6) δ : 2.39 (3H, s, CH_3); 7.57 (2H, s, H-2+H-6); 7.69 (4H, m); 9.56 (1H, bs, OH). *^{13}C NMR* (DMSO-*d*6) δ : 14.5, 113.2, 115.3, 117.3, 122.0, 122.3, 124.5, 128.7, 133.5, 134.4, 135.1, 140.1, 140.2, 160.8, 165.9, 186.8, 186.9 .

and concentrated hydrochloric acid was added (3mL). After stirring for 10min, the precipitate that formed was filtered under vacuum and recrystalized from ethanol; yield 0.34g (69%). The spectral data for the 1,3-dithiol-2-ylidene derivatives **9a-d** are presented in table 1.

The synthetic strategy for 1,3-dithiol-2-ylium derivatives involves two steps: the synthesis of the corresponding phenacyl carbodithioates, followed by their cyclo-condensation under acid conditions [28-32]. The reactions of the salts of dithiocarbamic acid with *a*-bromophenones lead to various substituted phenacyl carbodithioates, under mild reaction conditions. Following this reaction pathway, described in scheme 2, 1-(3,5-dibromo-4-hydroxyphenyl)-1-oxapropan-2-yl-*N,N*-dimethyldithiocarbamate (**5**) has been synthesized by reacting 2-bromo-1-(3,5-dibromo-4-hydroxyphenyl) propan-1-one (**3**) with sodium *N,N*-dimethyldithio-carbamate (**4**), in acetone under heating. The key intermediate 2-bromo-1-(3,5-dibromo-4-hydroxyphenyl) propan-1-one (**3**) has been synthesized according to the literature procedure (scheme 1), through a consecutive bromination sequence of 1-(4-hydroxyphenyl)propan-1-one (**1**) and 1-(3,5-dibromo-4-hydroxyphenyl)propan-1-one (**2**), respectively [33].

The *N,N*-dimethyldithiocarbamate (**5**) has been obtained as colorless crystals in 80% isolated yields. The structure of this compound has been proved by analytical and spectral data. The ^{1}H NMR spectra indicate the presence of new signals at 3.38 and 3.56ppm belonging to the methyl protons in *N,N*-dimethylamino moiety. The different chemical shifts for the two methyl groups indicate a restricted free rotation around the carbon-nitrogen bond in dithiocarbamic group. ^{13}C NMR spectra indicate the appearance of a new signal at 193.4 ppm, attributed to the thiocarbonyl group.

As mentioned before, the second step for the synthesis of 1,3-dithiol-2-ylium derivatives consist in acid catalyzed cyclocondensation of phenacyl carbodithioates. Using a mixture of concentrated sulfuric acid-glacial acetic acid (1:3 v/v) the cyclization of dithiocarbamates **5** takes place under mild reaction conditions (10 min at 80°C). The resulted 1,3-dithiolium hydrogen sulfate is a water soluble compound. Because of this property 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-4-hydroxyphenyl)-5-methyl-2-*N,N*-dimethylamino-1,3-dithiol-2-ylium perchlorate (**6**) as colorless crystals, in 87% yield (scheme 2). The IR spectra revealed the disappearance of the absorption band corresponding to the carbonyl group (1678 cm^{-1}) and the presence of a new, strong and broad, absorption band at 1049-1105 cm^{-1}, corresponding to the perchlorate anion. ^{1}H NMR spectra of 1,3-dithiol-2-ylium perchlorates indicate the absence of the α-carbonyl hydrogen from compounds **5** (5.68ppm). Is worthy to note the high acidity of phenolic hydrogen, with a chemical shift of 10.69 ppm. ^{13}C NMR spectra also support the cyclization of dithiocarbamates **5** to the corresponding of 1,3-dithiolium salts by the disappearance of the carbonyl and thiocarbonyl atoms from dithiocarbamates spectra and the appearance of a new signal at a very low field (183.9ppm) which correspond to the electron deficient C(2) atom.

Treatment of 4-(3,5-dibromo-4-hydroxyphenyl)-5-methyl-2-*N,N*-dimethylamino-1,3-dithiol-2-ylium perchlorate (**6**), under heterogeneous conditions, with saturated aqueous sodium hydrogen carbonate solution provides 2,6-dibromo-4-[5-methyl-2-*N,N*-dimethylamino-1,3-dithiol-2-ylium-4-yl]phenolate (**7**), in quantitative yields as yellow compounds (scheme 3). The presence of a hydroxy substituent in the *para*-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 [27], 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 [34, 35]. As already mentioned, phenolate **7** have been isolated as a yellow solid that present the features of mesoionic compounds [36]. 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 **7** with 70% $HClO_4$ regenerates the 1,3-dithiolium perchlorate **6** 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 [26]. In order to synthesize the target 1,3-dithiol-2-ylidene derivatives mesoionic phenolate **7** were reacted with carbanions derived from various methylene active compounds (scheme 3). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) in acetonitrile was used as a base to extract a proton from the active methylene moiety. DBU is a strong enough base for this purpose being also a weak nucleophile; this property avoid the nucleophilic interaction with the 1,3-dithiolium ring as a competing reaction. The reaction of mesoionic phenolate **7** with thus generated *C*-nucleophiles from methylene active compounds **8a-d** provided 1,3-dithiol-2-ylidene derivatives **9a-d** in good to excellent isolated yields (table 1). An alternative synthetic procedure involves the 1,3-dithiolium perchlorate **6** instead of the mesoionic phenolate **7** in a one step procedure for reactions described in scheme 3. In that case, one extra equivalent of DBU is needed in order to convert, in a first step, the salt to mesoionic compound.

A reasonable reaction mechanism has been previously proposed by us [37]. 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 *N,N*-dimethylamino moiety and the formation of the double bond.

The formation of the 1,3-dithiol-2-ylidene derivatives **9a-d** 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 **9a-d**. In the case of compound **9d**, a new multiplet can be found in the aromatic area, corresponding to the benzenic 1,3-indandione moiety. The regeneration of the phenolic group (see experimental procedure) 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 (191-193 ppm) and ester groups (166 ppm) confirm the structures of the new 1,3-dithiol-2-ylidene derivatives.

Conclusions

The synthesis of new 4-(3,5-dibromo-4-hydroxyphenyl)-5-methyl-1,3-dithiol-2-ylidene derivatives has been performed by reacting 2,6-dibromo-4-[5-methyl-2-*N*,*N*-dimethylamino-1,3-dithiol-2-ylium-4-yl]phenolate with various active methylene compounds. The latter have been *in situ* converted into nucleophiles, using DBU, a non-nucleophilic base. The 1,3-dithiol-2-ylium compounds have been obtained from the reaction of the substituted a-bromo-4-hydroxypropiophenone with sodium *N*,*N*-dimethyl-dithiocarbamate. The newly obtained derivatives were characterized by NMR spectrometry and IR spectroscopy.

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References

1.ISHIGURO, T., YAMAJI, K., SAITO, G., Organic Superconductors (Springer Series in Solid-State Sciences), 2nd edition, Ed. FULDE, P., Springer, Berlin, vol. 88, 1998.
2.FERRARIS, J., COWAN, D.O., WALATKA Jr., V., PERLSTEIN, J.H., J. Am. Chem. Soc., **95**, 1973, p. 948.
3.JEROME, D., MAZAUD, A., RIBAULT, M., BECHGAARD, K., J. Phys. Lett., **41**, 1980, p. L95.
4.BECHGAARD, K., CARNEIRO, K., RASMUSSEN, F.B., OLSEN, M., RINDORF, G., JACOBSEN, C.S., PEDERSEN, H.J., SCOTT, J.C., J. Am.Chem. Soc., **103,** 1981, p. 2440.
5.YAMADA, J., SUGIMOTO, T., TTF Chemistry - Fundamentals and Applications of Tetrathiafulvalene, Kodansha-Springer, 2004.
6.ADACHI, T., OJIMA, E., KATO, K., KOBAYASHI, H., MIYAZAKI, T., TOKUMOTO, M., KOBAYASHI, A., J. Am. Chem. Soc., **122**, 2000, p. 3238.
7.OTSUBO, T., TAKIMIYA, K., Bull. Chem. Soc. Jpn., **77**, 2004, p. 43.
8.YAMADA, J.-i., J. Mater. Chem., **14**, 2004, p. 2951.
9.WADA, A., NISHIDA, J.-i., MAITANI, M.M., WADA, Y., YAMASHITA, Y., Chem. Lett., **43**, 2014, p. 296.
10.BAHRIN, L.G., LUCA, A., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 199.
11. BIRSA, M.L., SANDU, I., BAHRIN, L.G., Rev. Chim. (Bucharest), **65**, no. 2, 2014, p. 174.
12.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.
13.SARBU, L.G., APOSTU, M.O., SANDU, I.G., MANEA, L.R., BAHRIN, L.G., Rev. Chim. (Bucharest), **65**, no. 11, 2014, p. 1327.
14.BAHRIN, L.G., ASAFTEI, I.V., SANDU, I.G., SARBU, L.G., Rev. Chim. (Bucharest), **65**, no. 9, 2014, p. 1046.
15.SARBU, L.G., LUNGU, N.C., BALAN, A., BAHRIN, L.G., Rev. Chim. (Bucharest), **65**, no. 10, 2014, p. 1135.
16.BAHRIN, L.G., LUNGU, N.C., FORNA, N.C., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **64**, no. 11, 2013, p. 1343.
17.SARAVANAKUMARA, R., MARKOPOULOS, G., BAHRIN, L.G., HOPF, H., Synlett, **24**, 2013, p. 453.
18.BAHRIN, L.G., JONES, P.G., HOPF, H., Beilstein J. Org. Chem., **8**, 2012, p. 1999.
19.GOSAV, S., PRAISLER, M., BIRSA, M.L., Int. J. Mol. Sci., **12**, 2011, p. 6668.
20.GOSAV, S., BIRSA, M.L., Rom. Rep. Phys., **66**, 2014, p. 411.
21.SARBU, L.G., SANDU, I., BAHRIN, L.G., BALAN, A., APOSTU, M.O., Rev. Chim. (Bucharest), **66**, no. 1, 2015, p. 55.
22.SARBU, L.G., BAHRIN, L.G., Acta Chem. Iasi, **21**, 2013, p. 47.
23.MARIN, L., ARVINTE, A., Mat. Plast., **50**, no. 1, 2013, p. 23.
24.SERBEZEANU, D., VLAD-BUBULAC, T., HAMCIUC, C., AFLORI, M., BRUMA, M., Mat. Plast., **48**, no. 2, 2011, p. 117.
25.BAHRIN, L.G., APOSTU, M.O., BIRSA, M.L., STEFAN, M., Bioorg. Med. Chem. Lett., **24**, 2014, p. 2315.
26.BIRSA, M.L., Synth. Commun., **33**, 2003, p. 3071.
27.BIRSA, M.L., GANJU, D., J. Phys. Org. Chem., **16**, 2003, p. 207.
28.SCHUKAT, G., RICHTER, A.M., FANGHANEL, E., Sulfur Rep., **7**, 1987, p. 155.
29.SCHUKAT, G., FANGANEL, E., Sulfur Rep., **14**, 1993, p. 245.
30.SADEKOV, I.D., RIVKIN, B.B., MINKIN, V.I., Sulfur Rep., **15**, 1993, p. 103.
31.BUHACEANU, R., LUNGU, N.C., FORNA, N.C., ASAFTEI, I.V., CHIRITA, P., BIRSA, M.L., Rev. Chim. (Bucharest), **64**, no. 8, 2013, p. 802.
32.BUHACEANU, R., LUNGU, N.C., FORNA, N.C., ASAFTEI, I.V., CHIRITA, P., BIRSA, M.L., Rev. Chim. (Bucharest), **64**, no. 9, 2013, p. 960.
33.BIRSA, M.L., TIRON, R., IGNAT, L., An. St. Univ. Al. I. Cuza Iasi, s. Chimie, **8**, 2000, p. 335.
34.BIRSA, M.L., ASAFTEI, I.V., Monat. Chem., **139**, 2008, p. 1433.
35.SARBU, L.G., LUNGU, N.C., ASAFTEI, I.V., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 3, 2014, p. 325.
36.ATHAYDE FILHO, P.F., MILLER, J., SIMAS, A.M., Synthesis, **2000**, p. 1565.
37.BAHRIN, L.G., CRACIUN, B.F., SANDU, I., BIRSA, M.L., Rev. Chim. (Bucharest), **65**, no. 5, 2014, p. 525.

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