ACTA CHEMICA IASI, **26_2**, 153-168 (2018)

DOI: 10.2478/achi-2018-0010

2-*N,N*-DIALKYLAMINO-1,3-DITHIOLIUM SALTS

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Abstract: The synthesis of 2-*N,N*-dialkylamino-1,3-dithiolium salts is reviewed.

***Keywords*:** Ditiocarbodithioates, 1,3-dithiolium salts, tetrathiafulvalenes.

Introduction

Over the past 50 years, the chemistry of 1,3-dithiolium salts has known a significant development. The discovery of the unusual solid-state electrical conductivity properties of the tetrathiafulvalene (TTF) and tetracyanochinodimethane (TCNQ) charge transfer complex stimulated the expansion of research concerning 1,3-dithiolium salts, which are important intermediates in the synthesis of tetrathiafulvalene derivatives. The properties of organic conductors were recognized worldwide in 2000 by awarding the Nobel Prize in Chemistry to three researchers who revolutionized the field of organic conductive polymers.

The 1,3-dithiolium cations **2** are pentaatomic heterocycles containing two sulfur atoms in the 1 and 3 positions. These ions can be formally derived from the corresponding 1,3-dithiols **1** by removing a

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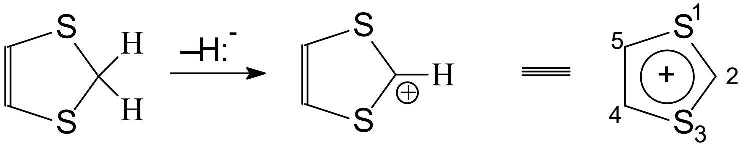
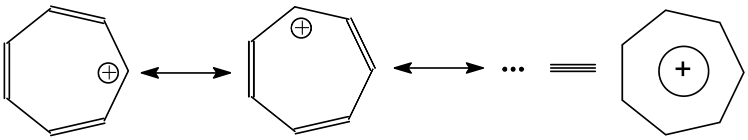
hydride ion or the tropylium ion, by replacing two carbon-carbon double bonds (1 and 5) with two sulfur atoms.

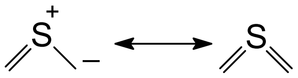


1 **2** **3**



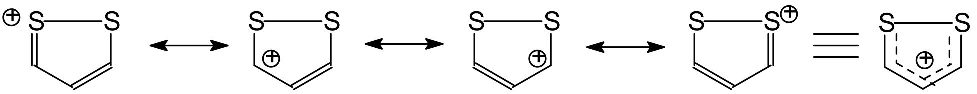
In both cases, a cyclic system containing 6 π electrons is generated which, according to Hückel's rule, should be very stable and exhibit “aromatic” properties.

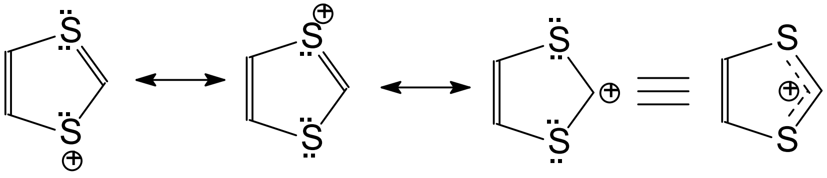
By analyzing the structure of these heterocycles, a number of interesting formulations, which are represented either by dipolar structures or by covalent structures, involves the presence of tetravalent sulfur. The bonds in this valence state, S(IV), involves the participation of 3*d* orbitals of the sulfur atoms. The following dipole can be represented either by a dipolar formulation or by a covalent formula involving the presence of tetravalent sulfur:



But this leads to the following question: are the covalent structures involving tetravalent sulfur necessary to properly describe the structure of dithiolium cations? Several spectroscopic and theoretical studies concluded that the bond that requires the participation of the 3*d* orbital sulfur is not involved in the structure of these compounds.

As with the 1,2-dithiolium cations series, 1,3-dithiolium cations may adopt two types of structures, namely sulfonium and carbenium cations, with the exception that the positive charge is delocalized only to a carbon atom (-S-C-S-), the mesomeric formulation **3** being in fact not in agreement with the properties exhibited by these compounds. Therefore, in the representation of 1,3-dithiolium cations, structure **4** will be used, while the issue concerning the aromatic character and positive charge delocalization over the entire heterocycle will be addressed later.





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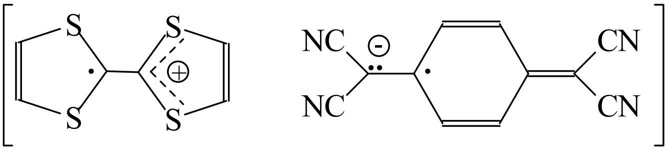
The synthesis and reactivity of 1,3-dithiolium salts, as well as sulfur, selenium and condensed cycles analogues, has been updated from the perspective of condensation, cyclization, protonation and elimination reactions.[1-16]

Synthesis of 1,3-dithiolium salts

Over the past 50 years, the chemistry of 1,3-dithiolium salts has known a significant development. The discovery of the unusual solid-state electrical conductivity properties of the tetrathiafulvalene (TTF) and tetracyanochinodimethane (TCNQ) charge transfer complex **5** stimulated the expansion of research regarding 1,3-dithiolium salts, which are important intermediates in the synthesis of tetrathiafulvalene derivatives.[17-20]



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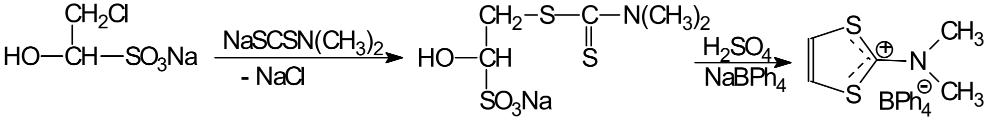
New synthetic methods for unsubstituted 1,3-dithiolium salts and for a wide range of 2-aryl, 2-alkyl, 2-methylthio or 2-amino substituted derivatives have been achieved. Classification of 1,3-dithiolium salts was realized according to the type of substituent at the 2 position, considering the fact that its nature specifically affects the reactivity of these salts.

Generally, dithiolium salts (halides, hydrogen sulfates, perchlorates, tetrafluoroborates, etc.) are stable, crystalline compounds readily purified by recrystallization. The perchlorates, which sometimes decompose violently on heating, are not suitable for large scale preparations, however due to high melting points and the fact that they are easily purified by recrystallization, they are often used in research.

Treatment of sodium *N*,*N*-dimethyldithiocarbamate with an equimolecular amount of the chloroacetaldehyde adduct with sodium bisulfite and then with sulfuric acid and sodium tetraphenylborate results in the formation of 2-*N,N*-dimethylamino-1,3-dithiolium tetraphenylborate **6**:[21]



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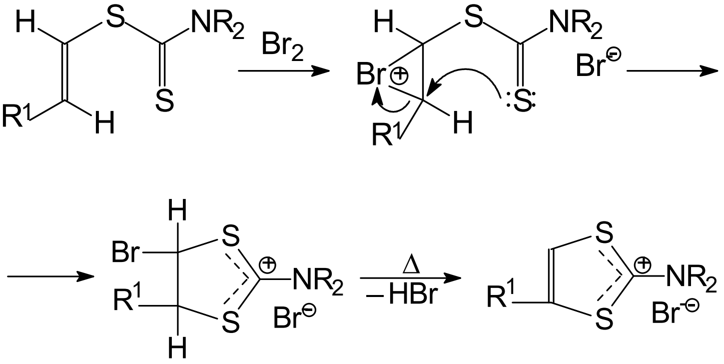
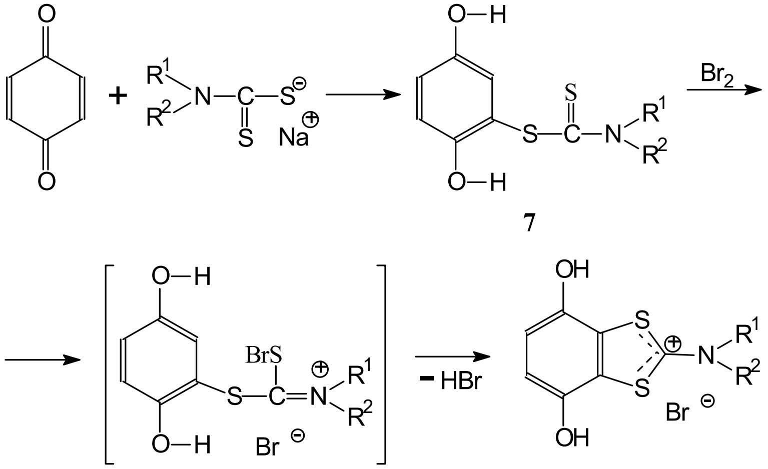
S-Vinyl-*N*,*N*-dialkylaminocarbodithioates undergo a cyclization reaction in the presence of bromine, followed by the thermal elimination of hydrobromic acid:[22]



Treatment of *p*-benzoquinone with an *N*,*N*-dialkylaminocarbodithioate in acetic acid rapidly leads to 1,4-dihydroxy-2-*N*,*N*-dialkylaminocarbodithioate **7**. Reaction of compound **7** with bromine in chloroform results in the corresponding 1,3-benzodithiolium salt **8** through a mechanism which involves the initial addition of bromine to the thiocarbonyl sulfur atom, followed by cyclization:[23]



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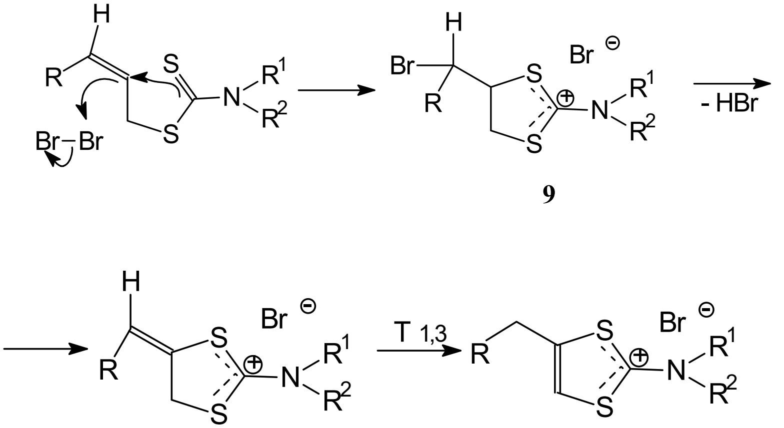
The thermal decomposition of 2-dialkylamino-4-(α-bromoalkyl)-1,3-dithiolane bromide **9**, prepared brominating allyl *N,N*-dialkyldithiocarbamates, leads to the corresponding 4-alkyl-2-dialkylamino-1,3-dithiolium salts **11** in good yields.[24] Initially, the reaction mechanism involves a 1,2-dehydrobromination of 2-dialkylamino-4-(α-bromoalkyl)-1,3-dithiolanium bromide **9** to the corresponding substituted 4-alkylidene-1,3-dithiolium bromide **10**. This interpretation is supported by the failure of the thermal decomposition reaction of 4-bromomethyl-4-methyl-1,3-dithiolanium bromide, which no longer leads to the corresponding 1,3-dithiolium salt (a widening of the cycle occurs), because the presence of a substituent instead of the hydrogen at the 4 position makes the dehydrobromination reaction impossible. Subsequently, 4-alkylidene-1,3-dithiolanium bromide undergoes a 1,3-prototropic rearrangement (three carbon tautomerism) resulting in the corresponding 1,3-dithiolium salt **11**:

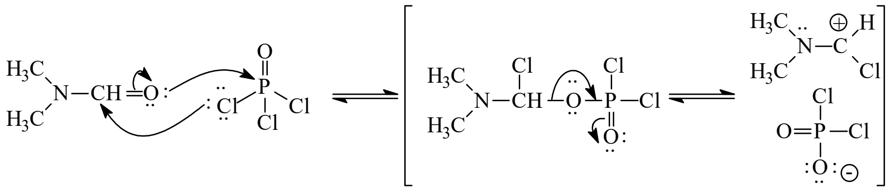


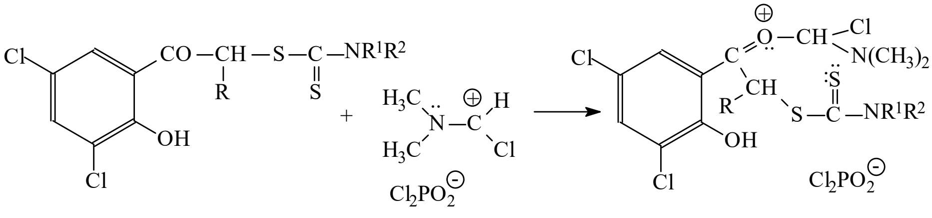
R = H ; $R^1 = R^2 = CH_3$ R = H ; $R^1 = R^2 = C_2H_5$ R = CH_3 ; $R^1 = R^2 = CH_3$

10 **11**

The attempt to obtain 2-dialkylamino-1,3-dithiolium salts by cyclization of phenacyl *N,N*-dialkylaminocarbodithioates under the Leaver-Robertson[25] reaction conditions (cyclization in ethereal solution saturated with hydrogen sulfide) resulted in a failure.[26] However, the modification of the reaction conditions turned *N,N*-dialkylaminocarbodithioates into important precursors of 2-(*N,N*-dialkylamino)-1,3-dithiolium salts. Thus, in the presence of 98% sulfuric acid, phosphorus pentasulfide and tetrafluoroboric acid,[27] 70% perchloric acid or Vilsmeier reagent, these salts are readily obtained.

In 1987, Al. Cascaval reported the synthesis of 2-dialkylamino-1,3-dithiolium salts as perchlorates **13**,[28] by the action of the Vilsmeier reagent (under Harnisch reaction conditions) on the corresponding *N,N*-dialkylaminocarbodithioates following the mechanism below:





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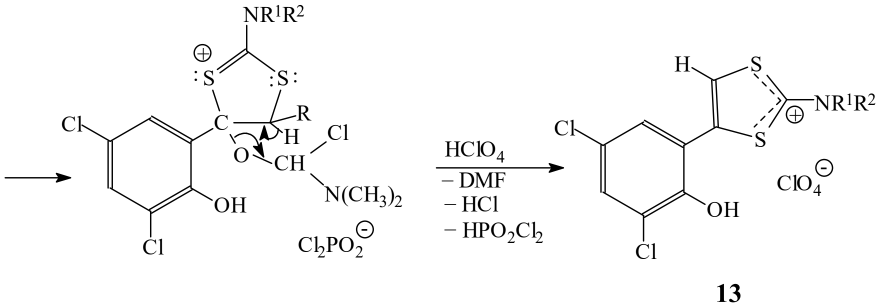

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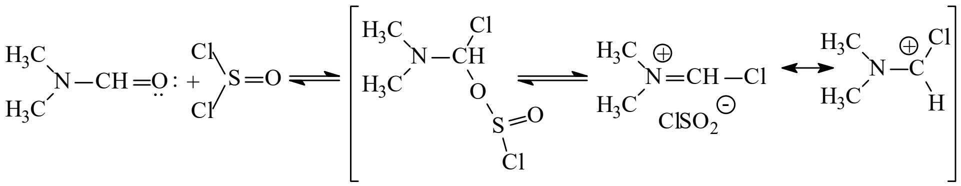
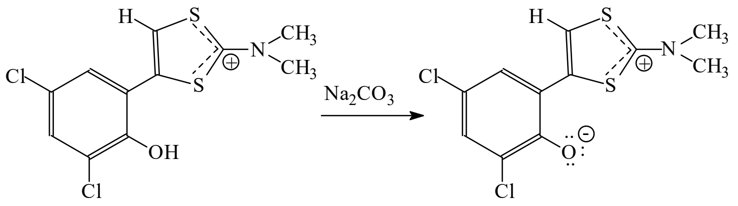
In the first step, the intermediate **12** is formed through a d^{0} - a^{1} interaction. A new d^{0} - a^{1} interaction takes place in this intermediate, the donor being the thiocarbonyl group through a non-bonding pair of electrons from the sulfur atom, and the acceptor is the carbon atom of the carbonyl group. Electrocyclic elimination of hydrochloric acid, dimethylformamide followed by addition of perchloric acid leads to 4-(3',5'-dichloro-2'-hydroxyphenyl)-2-(*N*,*N*-dialkylamino)-1,3-dithiolium perchlorate **13**, with a very good yield.

Modification of the above synthesis by replacing phosphorus oxychloride with thionyl chloride leads, under the same experimental conditions, to the same 2-(*N*,*N*-dialkylamino)-1,3-dithiol perchlorates **13**. Addition of a saturated sodium carbonate solution to the reaction mixture instead of perchloric acid results in the corresponding mesoionic compounds of these salts, 2-dimethylamino-4-(3,5-dichloro-2-hydroxyphenyl)-1,3-dithiolium anhydro-hydroxide (Iasinones) **14**.[29] Thus, the solubilisation of 2-(*N*,*N*-dimethylaminothiocarbonylthio)-1-(3,5-dichloro-2-hydroxyphenyl)-1-ethanone in dimethylformamide at room temperature, under stirring, followed by slow addition of thionyl chloride and then neutralizing the acidic solution with a saturated sodium carbonate solution yields the corresponding Iasinone:





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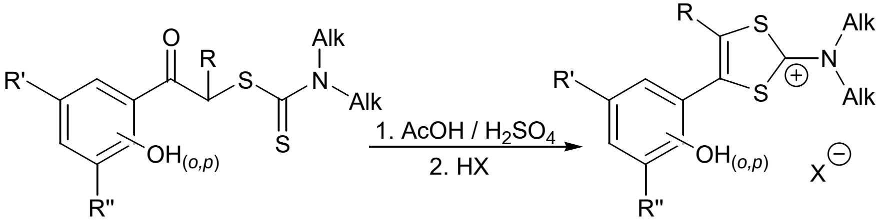
The experimental method described above has been improved in terms of milder reaction conditions and higher yields by using a sulfuric acid: acetic acid (1: 3 v/v) mixture as cyclization agent. A wide variety of 1,3-dithiolium salts **15** was synthesized from the corresponding phenacyl dithiocarbamates.[30-65] The corresponding 1,3-dithiolium phenolates exhibit a negative solvatochromism.[66]



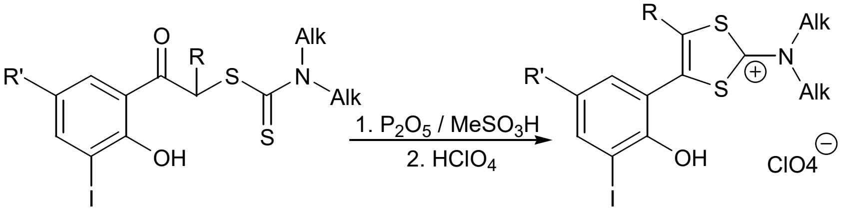
R = H, Me, Et; R' = H, Me, Br; R'' = H, Me, Br; X = ClO_4, BF_4, HSO_4, Cl

15

The synthesis of 1,3-dithiolium derivatives containing iodine was performed under different experimental conditions. If the synthesis of phenacyl carbodithioates does not raise any particular problems, their cyclization into the corresponding 1,3-dithiolium salts is an important experimental obstacle. This is because the use of H_2SO_4 conc. - CH_3COOH gl. (1: 3 vol.) at 80 °C for the cyclization of carbodithioates **16** results in the irreversible degradation of the substrate, sometimes with the release of molecular iodine. As expected, considering the much tougher reaction conditions, neither does the use of cyclization agents commonly employed in the synthesis of 1,3-dithiolium salts (P_4S_{10} + HBF_4, HBF_4, 70% $HClO_4$, Vilsmeier reagent). Experimental observations have allowed us to conclude that the responsibility for these failures rests, on one hand, on the nature of the cyclization agent used and on the other hand, on the temperature at which the reaction takes place.

In view of this, the use of a “superacid” mixture of P_2O_5 - CH_3SO_3H (1: 10) was attempted. This reagent is successfully used as a replacement for polyphosphoric acid in some dehydration reactions, in the Beckmann rearrangement, the Schmidt rearrangement, and in the alkylation and acylation reactions of olefinic and aromatic systems.[67]

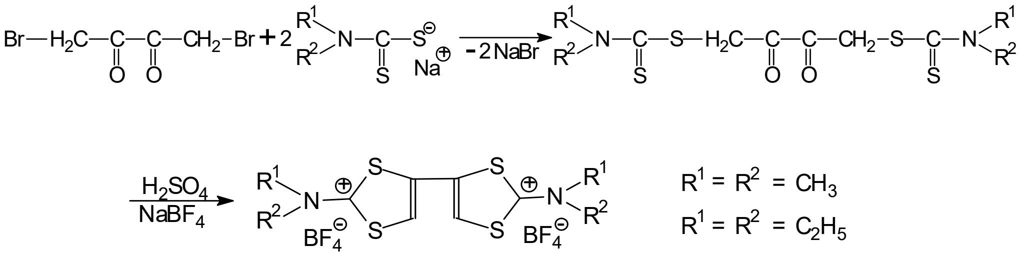
Thus, by suspending carbodithioates **16** in this reagent and maintaining the reaction mixture at temperatures between 40 and 50 °C the formation of a homogeneous solution containing the corresponding 1,3-dithiolium cation occurs.[68,69] Addition of water and 70% perchloric acid allows the isolation of perchlorates **17** as white solids.



R = H, Me; R' = H, Me, I

16 **17**

The use of 1,3-dithiolium salts as intermediates in the synthesis of tetrathiafulvalenes led to the need to obtain two dithiolium moieties linked directly, or *via* an aliphatic or aromatic chain. Thus, treatment of 1,4-dibromo-2,3-butanedione with *N,N*-dialkylaminocarbodithioates followed by cyclization with sulfuric acid and addition of an aqueous solution of sodium tetrafluoroborate results in 4,4'-bis-(2-dialkylamino)-1,3-ditiolium tetrafluoroborates **18**[70]:



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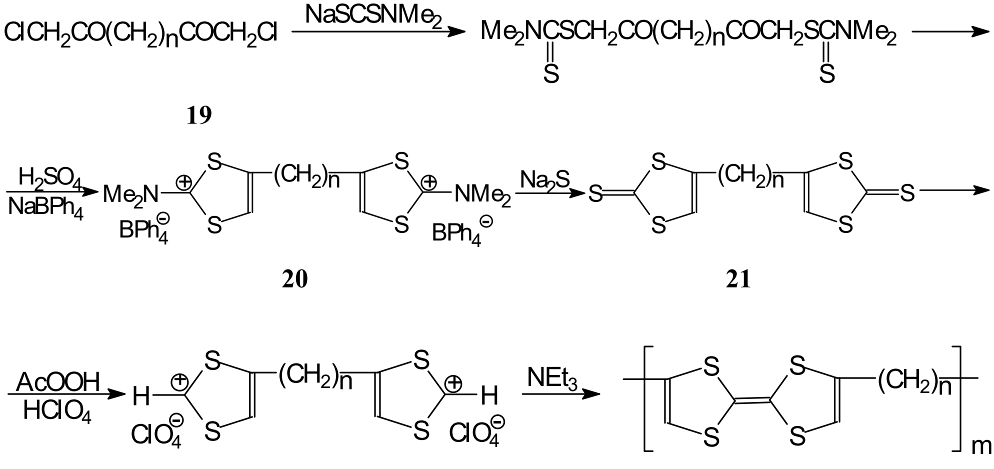
Ueno et al. reveals the synthesis of some 1,3-dithiolium rings linked by an aliphatic chain specifically chosen so as not to cause a decrease in the donor character of the polymer.[71] The synthetic pathway involves the use of a bis(*β*-ketochloride) **19** which is reacted with two equivalents of sodium *N,N*-dimethyldithiocarbamate. The *N,N*-dialkylaminocarbodithioate formed is then treated with sulfuric acid and sodium tetraphenylborate, after which, without isolating the 1,3-dithiolium salt **20**, the reaction mixture is treated with an excess of sodium sulfide to give the corresponding bis(1,3-dithiol-2-thione) **21**. Treatment of compound **21** with peracetic acid, perchloric acid and then with triethylamine results in the polymer **22** containing the tetrathiafulvalene moiety in its structure:



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Conclusions

The synthesis of 2-*N,N*-dialkylamino-1,3-dithiolium salts has been reviewed. These compounds are valuable precursors for tetrathiafulvalene derivatives.

Acknowledgements

This work was supported by Ministery of Research and Innovation, CNCS - UEFISCDI project number PN-III-Pl-l.1-PD-2016-0962, within PNCDI III.

References

1. Schukat, G.; Fanghänel, E. 1,3-Dithiolium Salts, Se and Te Analogues, and Benzoannulated Analogues. *Science of Synthesis* **2002**, *11*, 191-229.
2. Meziere, C.; Allain, M.; Oliveras-Gonzalez, C.; Cauchy, T.; Vanthuyne, N.; Sarbu, L.G.; Birsa, L.M.; Pop, F.; Avarvari, N. Tetrathiafulvalene-[2.2]paracyclophanes: Synthesis, crystal structures, and chiroptical properties. *Chirality* **2018**, *30*, 568-575.
3. Babii, C.; Mihalache, G.; Bahrin, L.G.; Neagu, A.N.; Gostin, I.; Mihai, C.T.; Sarbu, L.G.; Birsa, L.M.; Stefan, M. A novel synthetic flavonoid with potent antibacterial properties: In vitro activity and proposed mode of action. *Plos One* **2018**, *13*, 1-15.
4. Bahrin, L.G.; Sarbu, L.G.; Jones, P.G.; Birsa, L.M.; Hopf, H. [2.2]Paracyclophane-Bis(triazole) Systems: Synthesis and Photochemical Behavior. *Chem. Eur. J.* **2017**, *23 (50)*, 12338-12345.
5. Gorodea, I.A.; Sandu, I.; Sarbu, L.G. Novel 4-(3-Bromo-2-hydroxy-5-methylphenyl)-1,3-Dithiol-2-ylidene Derivatives. *Rev. Chim. (Bucharest)* **2017** *68*, 1988-1991.
6. Matei, M.; Sandu, I.; Birsa, M.L.; Sarbu, L.G.; Simion, L. New 4-(4-Hydroxyaryl)-5-Methyl-1,3-Dithiol-2-ylidene Derivatives. *Rev. Chim. (Bucharest)* **2017**, *68*, 81-84.
7. Pavel, S.; Hopf, H.; Jones, P.G.; Asaftei, I.V.; Sarbu, L.G.; Birsa, L.M. Click reactions with *pseudo-geminal* bis(azido-methylene)[2.2]paracyclophane. *Monatsh. Chem.* **2016**, *147*, 2179-2183.
8. Toader, E.; Bahrin, L.G.; Jones, P.G.; Hopf, H.; Sarbu, L.G.; Stoleriu, G. Synthesis of New Morpholine Containing Flavonoids with Potential Biological Applications. *Rev. Chim. (Bucharest)* **2016**, *67*, 1520-1522.
9. Dirtu, D.; Lungu, N.C.; Chirita, P.; Sandu, I.G.; Birsa, M.L.; Earar, K.; Sarbu, L.G. Synthesis of Novel 4-(3,5-Dibromo-2-hydroxyphenyl)-5-Methyl-1,3-Dithiol-2-ylidene Derivatives. *Rev. Chim. (Bucharest)* **2016**, *67*, 534-537.
10. Sarbu, L.G.; Bahrin, L.G.; Jones, P.G.; Birsa, M.L.; Hopf, H. [2.2]Paracyclophane derivatives containing tetrathiafulvalene moieties. *Beilstein J. Org. Chem.*, **2015**, *11*, 1917-1921.
11. Sarbu, L.G.; Hopf, H.; Grunenberg, J.; Birsa, M.L. Reduction of Pseudo-geminal Bis(ethynyl)-Substituted [2.2]Paracyclophanes. *Synlett*, **2015**, *26*, 87-90.

12. Sarbu, L.G.; Hopf, H.; Jones, P.G.; Birsa, M.L. Selenium halide-induced bridge formation in [2.2]paracyclophanes. *Beilstein J. Org. Chem.*, **2014**, *10*, 2550-2555.

13. Sarbu, L.G.; Bicu, E.; Hopf, H.; Birsa, M.L. [2.2]Paracyclophane Substituted Indolizines. *Rev. Chim. (Bucharest)*, **2014**, *65*, 398-400.

14. Sarbu, L.G.; Birsa, A.; Hopf, H.; Birsa, M.L. New Bridges In [2.2]Paracyclophanes: The Interaction Of Chalcogenide Halides With *Pseudo-Geminal* Triple Bonds. *Phosphorus, Sulfur, and Silicon, and the Related Elements* **2011**, *186*, 1246-1250.

15. Sarbu, L.G.; Birsa, A.; Hopf, H.; Birsa, M.L. Heteroatom Bridged[2.2]Paracyclophanes As Enediyne Analogs. *Acta Chem. Iasi* **2010**, *18*, 186-193.

16. Sarbu, L.G.; Birsa, A.; Ignat, L.; Hopf, H.; Birsa, M.L. [2.2]Paracyclophanes: The Interaction of *Pseudo-Geminal* Bisacetylene with Water and Electrophiles. *Acta Chem. Iasi*, **2010**, *18*, 71-78.

17. Narita, M.; Pittman Jr, C.U. Preparation of Tetrathiafulvalenes (TTF) and their Selenium Analogs -Tetraselenafulvalenes (TSeF). *Synthesis* **1976**, 489-514.

18. Schukat, G.; Richter, A.M.; Fanghänel, E. Synthesis, Reactions, and Selected Physico-Chemical Properties of 1,3-and 1,2-Tetrachalcogenafulvalenes. *Sulfur Rep.* **1987**, *7*, 155-127.

19. Schukat, G.; Fanghänel, E. Synthesis, Reactions, and Selected Physico-Chemical Properties of 1,3- and 1,2-Tetrachalcogenafulvalenes. *Sulfur Rep.* **1993**, *14*, 245-383.

20. Diaz, M.C.; Illescas, B.M.; Martin, N.; Perepichka, I.F.; Bryce, M.R.; Levillain, E.; Viruela, R.; Orti, E. Electronic interaction in new π-extended tetrathiafulvalenes dimers. *Chem. Eur. J.* **2006**, *12*, 2709-2721.

21. Ueno, Y.; Nakayama, A.; Okawara, M. An Improved Method for Methoxymethylation of Alcohols under Mild Acidic Conditions. *Synthesis* **1975**, 276-277.

22. Hiratani, K.; Shiono, H.; Okawara, M. A New Synthetic Route To 1,3-Dithiolium Salts Involving Neighboring Group Participation Of Dithiocarbamate Group. *Chem. Lett.* **1973**, 867-870.

23. Harris, R.L.N.; Oswald, L.T. The addition of dithiocarbamic acids to p-benzoquinone. *Aust. J. Chem.* **1974**, *27*, 1309-1316.

24. Nakai, T.; Hiratani, K.; Okawara, M. Tri(hetero)substituted Carbonium Ions. XI. A Novel Synthetic Route to 2-Dialkylamino-4-alkyl-1,3-dithiolium Salts. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 827-828.

25. Leaver, D.; Robertson, W.A.H.; McKinnon, D.M. Synthesis of tetrathiafulvalenes. *J. Chem. Soc.* **1962**, 5104-5109.

26. Campaigne, E.; Jacobsen, N.W. Dithiolium Derivatives. I. 2-Dialkylamino-1,3-dithiolium Perchlorates. *J. Org. Chem.* **1964**, *29*, 1703-1708.

27. Takamizawa, A.; Hirai, K. Studies on 1, 3-Dithiolium Cations. I. A Novel Synthetic Method of 4-p-Substituted Phenyl Derivatives and Related Compounds. *Chem. Pharm. Bull.* **1969**, *17*, 1924-1930.

28. Cascaval, A. Compusi mezoionici. *Bul. Inst. Polit. Iasi* **1987**, *XXXIII*, fasc. 1-4, 47-50.

29. Cascaval, A. *Compuşi organici mezoionici: Sidnone, Münchnone, Iaşinone*, Ed. Univ. "Al.I. Cuza" Iaşi, **1995**.

30. Birsa, M.L. Dithiolium derivatives. I. *An. St. Univ. "Al.I. Cuza" Iasi* **1998**, *VI*, 57-64.

31. Birsa, M.L. Dithiolium derivatives. II. *An. St. Univ. "Al.I. Cuza" Iasi* **1999**, *VII*, 341-347.

32. Dirtu, D.; Asaftei, I.V.; Chirita, P.; Sandu, I.G.; Birsa, M.L.; Earar, K.; Sarbu, L.G. Synthesis of 1,3-Dithiol-2-ylium Salts by Functionalization of Some Toluenols. *Rev. Chim. (Bucharest)* **2015**, *66*, 2028-2030.

33. Chirita, P.; Asaftei, I.V.; Sandu, I.; Sarbu, L.G.; Lupu, V.V. Mesoionic 4-(2-Dialkylamino-1,3-dithiol-2-ylium-4-yl)phenolates. *Rev. Chim. (Bucharest)* **2017** *68*, 147-150.

34. Chirita, P.; Duinea, M.I.; Sandu, A.M.; Birsa, L.M.; Sarbu, L.G.; Baibarac, M.; Sava, F.; Popescu, M.; Matei, E. Inhibitory effect of three phenacyl derivatives on the oxidation of sphalerite (ZnS) in air-equilibrated acidic solution. *Corros. Sci.* **2018**, *138*, 154-162.

35. Asaftei, I.V.; Sandu, I.G.; Lungu, N.C.; Birsa, M.L.; Sarbu, L.G.; Ignat, M. Conversion of Butane-Butylene Mixtures over B(Al)-HZSM-5 Catalyst Prepared by Impregnation and over ZnO/HZSM-5 co-Catalyst Prepared by Mechanical Mixing. *Rev. Chim. (Bucharest)* **2016**, *67(5)*, 847-853.

36. Birsa, M.L. Synthesis of some 4-(2'-hydroxyaryl)-5-ethyl-2-(*N*,*N*-dialkylamino)-1,3-dithiolium salts. *Sulfur Lett.* **2003**, *26*, 155-162.

37. Asaftei, I.V.; Lungu, N.C.; Birsa, M.L.; Sarbu, L.G.; Ignat, M.; Sandu, I.G. Conversion of Light Hydrocarbons From Petroleum Refining Processes Over Zn-HZSM-5 (Nitrate) and Zn-HZSM-5 (Acetate) Catalyst A comparative study. *Rev. Chim. (Bucharest)* **2016**, *67(8)*, 1523-1528.

38. Goanta, M.; Ciobanu, A.S.; Birsa, A.; Asaftei, I.V.; Birsa, M.L. Synthesis of 4-(3-Bromo-2-Hydroxy-5-Methylphenyl)-2-Dialkylamino-1,3-Dithiolium Chlorides. *Acta Chem. Iasi* **2009**, *17*, 35-48.

39. Sarbu, L.G.; Bahrin, L.G. 3-Methylpiperidinyl Carbodithioates as Building Blocks for 1,3-Dithiolium Derivatives. *Acta Chem. Iasi* **2013**, *21*, 47-56.

40. Sarbu, L.G.; Birsa, M.L. Synthesis of Iodine Containing Mesoionic 2-(1,3-Dithiolium)phenolates. *Acta Chem. Iasi* **2011**, *19*, 125-135.

41. Bahrin, L.G. ; Jones, P.G. ; Hopf, H. Tricyclic flavonoids with 1,3-dithiolium substructure. *Beilstein J. Org. Chem.* **2012**, *8*, 1999-2003.

42. Sarbu, L.G.; Hrib, C.G.; Birsa, M.L. rac-1-(5-Bromo-2-hydroxyphenyl)-1-oxopropan-2-yl morpholine-4-carbodithioate. *Acta Cryst.* **2013**, *E69*, o1169.

43. Lungu, N.C., Sandu, I., Chirita, P., Birsa, M.L. New water soluble 1,3-dithiolium salt. *Rev. Chim. (Bucharest)* **2013**, *64*, 697-700.

44. Buhaceanu, R.; Lungu, N.C.; Forna, N.C.; Asaftei, I.V.; Chirita, P.; Birsa, M. L. A new class of mesoionic 4-(1,3-dithiol-2-ylium)phenolates. *Rev. Chim. (Bucharest)* **2013**, *64*, 803-807.

45. Buhaceanu, R.; Lungu, N.C.; Forna, N.C.; Asaftei, I.V.; Chirita, P.; Birsa, M.L. The influence of bromine substituent on optical properties of some 1,3-dithiolium derivatives. *Rev. Chim. (Bucharest)* **2013**, *64*, 960-964.

46. Bahrin, L.G.; Lungu, N.C.; Forna, N.C.; Sandu, I.; Birsa, M.L. Zwitterionic 3-(1,3-dithiol-2-ylium)phenolates. *Rev. Chim. (Bucharest)* **2013**, *64*, 1343-1346.

47. Sarbu, L.G.; Lungu, N.C.; Forna, N.C.; Birsa, M.L. Synthesis of 4-(2-hydroxyphenyl)-2-dialkylamino-1,3-dithiolium salts and corresponding mesoionic derivatives. *Rev. Chim. (Bucharest)* **2013**, *64*, 1404-1407.

48. Asaftei, I.V.; Lungu, N.C.; Birsa, L.M.; Sandu, I.G.; Sarbu, L.G.; Ignat, M. Performance of Ag-HZSM-5 Zeolite Catalysts in n-heptane Conversion. *Rev. Chim. (Bucharest),* **2017** *68*, 116-120.

49. Lungu, N.C.; Bahrin, L.G.; Asaftei, I.V.; Forna, N.C.; Sandu, I.; Birsa, M.L. Phenacyl 3-methylpiperidinyl carbodithioates as building blocks for 1,3-dithiolium derivatives. *Rev. Chim. (Bucharest)* **2014**, *65*, 181-184.

50. Sarbu, L.G.; Lungu, N.C.; Asaftei, I.V.; Sandu, I.; Birsa, M.L. New evidence for the mesoionic character of 2-(1,3-Dithiol-2-ylium)phenolates. *Rev. Chim. (Bucharest)* **2014**, *65*, 325-327.

51. Sarbu, L.G.; Bicu, E.; Belei, D. Synthesis of Mesoionic [2-(10*H*-phenothiazinyl)-1,3-dithiolium]phenolates. *Rev. Chim. (Bucharest)* **2014**, *65*, 249-252.

52. Bahrin, L.G.; Asaftei, I.V.; Sandu, I.G.; Sarbu, L.G. Synthesis of (4-Methylpiperazin-1-yl)carbodithioates and of their 1,3-Dithiolium Derivatives. *Rev. Chim. (Bucharest)* **2014**, *65*, 1046-1049.

53. Sarbu, L.G.; Lungu, N.C.; Balan, A.; Bahrin, L.G. Synthesis of Sulfur Containing Piperazine Derivatives with Potential Biological Activities. *Rev. Chim. (Bucharest)* **2014**, *65*, 1135-1138.

54. Sarbu, L.G.; Apostu, M.O.; Sandu, I.G.; Manea, L.R.; Bahrin, L.G. 1,3-Dithiol-2-ylium Compounds Derived from Substituted Butyrophenone *Rev. Chim. (Bucharest)* **2014**, *65*, 1327-1330.

55. Bahrin, L.G.; Apostu, M.O.; Birsa, M.L.; Stefan, M. The antibacterial properties of sulfur containing flavonoids. *Bioorg. Med. Chem. Lett.* **2014**, *24*, 2315-2318.

56. Birsa, M.L.; Sandu, A.V.; Balan, A. Synthesis of new 1,3-dithiolium derivatives from 4-hydroxyacetophenones. *Rev. Chim. (Bucharest)* **2014**, *65*, 1435-1438.

57. Hrib, C.G.; Sandu, I.; Earar, K.; Birsa, M.L. Synthesis of new 1,3-dithiolium derivatives from propiophenones. *Rev. Chim. (Bucharest)* **2014**, *65*, 1453-1456.

58. Apostu, M.O.; Sandu, I.; Birsa, M.L.; Earar, K. Synthesis of novel 4-aryl-5-methyl-1,3-dithiolium derivatives. *Rev. Chim. (Bucharest)* **2015**, *66*, 39-42.

59. Sarbu, L.G.; Sandu, I.; Bahrin, L.G.; Balan, A.; Apostu, M.O. New Bromo Substituted 1,3-Dithiol-2-ylium Salts. *Rev. Chim. (Bucharest)* **2015**, *66*, 55-58.

60. Chirita, P.; Hrib, C.G.; Lungu, N.C.; Sarbu, L.G.; Earar, K. A New Class of 4-(Hydroxyaryl)-1,3-Dithiolium Chlorides. *Rev. Chim. (Bucharest)* **2015**, *66*, 1151-1153.

61. Hrib, C.G.; Chirita, P.; Sandu, I.G.; Asaftei, I.V.; Sarbu, L.G.; Earar, K. The Synthesis and X-Ray Structural Characterization of New 4-(5-Bromo-2-hydroxyphenyl)-1,3-Dithiol-2-ylium Perchlorates. *Rev. Chim. (Bucharest)* **2015**, *66*, 983-985.

62. Bahrin, L.G.; Jones, P.G.; Hopf, H.; Earar, K.; Birsa, M.L. Synthesis of new iodine containing 1,3-dithiol-2-ylium salts. *Rev. Chim. (Bucharest)* **2016**, *67*, 61-63.

63. Bahrin, L.G.; Jones, P.G.; Hopf, H.; Poroch, V.; Birsa, M.L. Synthesis of fluorine containing 1,3-dithiol-2-ylium salts. *Rev. Chim. (Bucharest)* **2016**, *67*, 481-484.

64. Bahrin, L.G.; Hopf, H.; Jones, P.G.; Sarbu, L.G.; Babii, C.; Mihai, A.C.; Stefan, M.; Birsa, M.L. Antibacterial structure–activity relationship studies of several tricyclic sulfur-containing flavonoids. *Beilstein J. Org. Chem.* **2016**, *12*, 1065-1071.

65. Bahrin, L.G.; Sarbu, L.G.; Hopf, H.; Jones, P.G.; Babii, C.; Stefan, M.; Birsa, M.L. The influence of halogen substituents on the biological properties of sulfur-containing flavonoids. *Bioorg. Med. Chem.* **2016**, *24*, 3166-3173.

66. Birsa, M.L.; Ganju, D. Synthesis and UV/Vis spectroscopic properties of new [2-(*N*,*N*-dialkylamino)-1,3-dithiolium-4-yl]phenolates. *J. Phys. Org. Chem.* **2003**, *16*, 207-212.

67. Eaton, P.E.; Carlson, G.R.; Lee, J.T. Phosphorus pentoxide-methanesulfonic acid. Convenient alternative to polyphosphoric. *J. Org. Chem.* **1973**, *38*, 4071-4073.

68. Birsa, M.L. A new approach to preparation of 1,3-dithiolium salts. *Synth. Commun.* **2001**, *31*, 1271-1275.

69. Birsa, M.L.; Asaftei, I.V. Solvatochromism of mesoionic iodo(1,3-dithiol-2-ylium-4-yl)phenolates. *Monat. Chem.* **2008**, *139*, 1433-1438.

70. Andersen, J.R.; Patel, V.V.; Engler, E.M. Bis-1,3-dithiole chemistry: Synthesis of compounds containing the 4,4′bis-(1,3-dithiole) unit. *Tetrahedron Lett.* **1978**, 239-242.

71. Ueno, Y.; Masuyama, Y.; Okawara, M. Synthesis and Complex Formation of Macromolecules Having Tetrathiofulvalene Structure. *Chem. Lett.* **1973**, 603-606.