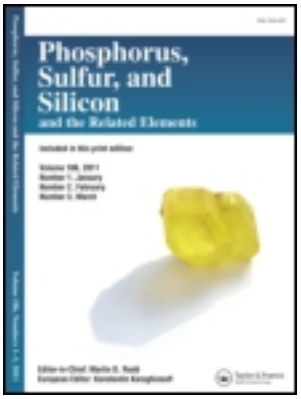


Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Synthesis of New Symmetric Disubstituted Dithioether Dithiols

Moufida Romdhani-Younes [a], Ines Gara [a], Amine Mezni [b] & Mohamed Moncef Chaabouni [a]

[a] Laboratoire de Chimie Organique Structurale, Département de Chimie, Faculté des Sciences de Tunis, Université Tunis El Manar, Tunis, Tunisia

[b] Unité de Recherche Synthèse et Structure des Matériaux Inorganiques 99/UR12-30, Département de Chimie, Faculté des Sciences de Bizerte, Jarzouna, Tunisia

Accepted author version posted online: 02 Mar 2012.Version of record first published: 19 Jun 2012.

To cite this article: Moufida Romdhani-Younes , Ines Gara , Amine Mezni & Mohamed Moncef Chaabouni (2012): Synthesis of New Symmetric Disubstituted Dithioether Dithiols, Phosphorus, Sulfur, and Silicon and the Related Elements, 187:9, 1074-1081

To link to this article: http://dx.doi.org/10.1080/10426507.2012.668984

Phosphorus, Sulfur, and Silicon, 187:1074–1081, 2012

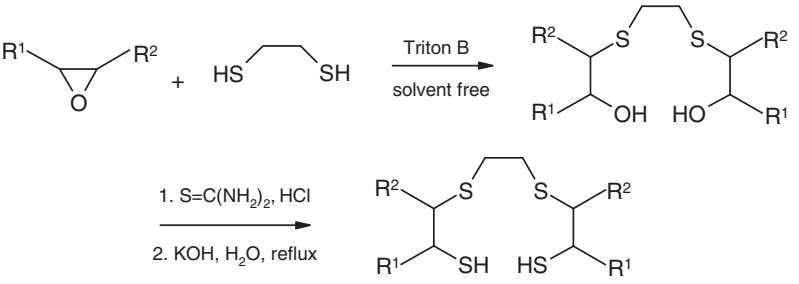
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2012.668984

SYNTHESIS OF NEW SYMMETRIC DISUBSTITUTED DITHIOETHER DITHIOLS

Moufida Romdhani-Younes,[1] Ines Gara,[1] Amine Mezni,[2] and Mohamed Moncef Chaabouni[1]

[1]*Laboratoire de Chimie Organique Structurale, Département de Chimie, Faculté des Sciences de Tunis, Université Tunis El Manar, Tunis, Tunisia*
[2]*Unité de Recherche Synthèse et Structure des Matériaux Inorganiques 99/UR12-30, Département de Chimie, Faculté des Sciences de Bizerte, Jarzouna, Tunisia*

GRAPHICAL ABSTRACT



R^1, R^2 = H, Me; H, Et; $(CH_2)_4$; H, CH_2OPh; H, Ph

Abstract *The β,β′-dihydroxydithioethers, derived from oxirane, have been converted into dithioethers dithiols in good yields. A colloidal solution of gold nanoparticles (AuNPs) with 5,8-dithiadodecane-3,10-dithiol was prepared and showed a good stability from tight binding offered by the thiol group on the Au surfaces.*

Keywords Epoxides; gold nanoparticles; hydroxy thioethers; thiols

INTRODUCTION

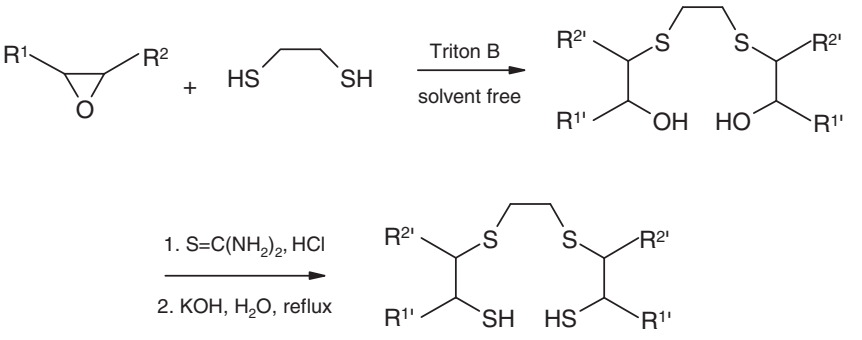
Since their discovery, thioetherthiol derivatives have been the subject of several studies.[1–4] Interest in such compounds is due to their applications in various fields such as the synthesis of polymers [5–8] and in the field of biochemistry.[9] The ability of thiols to penetrate in cellular tissues under physiological conditions and their fixation on DNA

Received 8 December 2011; accepted 8 February 2012.
Address correspondence to Moufida Romdhani-Younes, Laboratoire de Chimie Organique Structurale, Département de Chimie, Faculté des Sciences de Tunis, Université Tunis El Manar, 2092 Tunis, Tunisia. E-mail: moufida.romdhani@gmail.com

branches[10,11] demonstrates their importance in the medical field.[12,13] Compounds which contain two sulfur atoms are excellent precursors in organic synthesis,[14] particularly in the preparation of thiacrown ethers,[15–18] which are excellent chelating agents of some metallic ions.[19]

For instance, the incorporation of thiol groups into organic molecules allows their coordination to noble metal surfaces to form self-assembled monolayers (SAMs)[20,21] that have applications in molecular electronics[22–24] and in the synthesis of stable colloidal nanoparticles of noble metals, even under extreme conditions of pH and ionic strength due to strong interactions between gold and sulfur atoms.[25]

In the course of our work on the synthesis of sulfur containing compounds, we have prepared a number of polydentate ligands[26–29] exhibiting either a thioether or an oxathioether moiety as an additional donor function. We herein report the synthesis of a new series of symmetrically disubstituted dithioether dithiols **3a–e** (Table 1), accessible from substituted β,β'-dihydroxydithioethers **2a–e**. The starting compounds **2a–e** were prepared, as previously described,[27] from alkyl or aryl oxiranes in one step (Scheme 1).



1, 2, 3: a: R^1 = Me, R^2 = H; **b**: R^1 = Et, R^2 = H; **c**: R^1/R^2 = $(CH_2)_4$; **d**: R^1 = $PhOCH_2$, R^2 = H

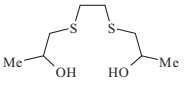
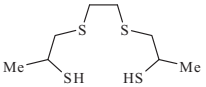
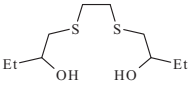
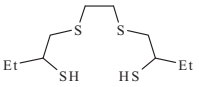
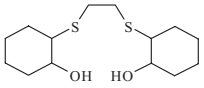
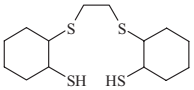
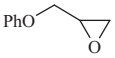
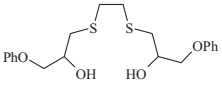
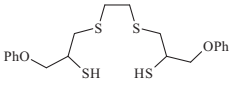
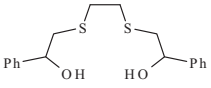
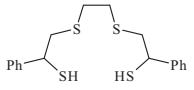
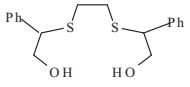
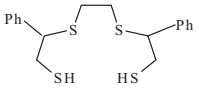
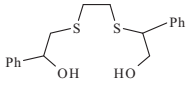
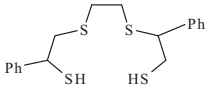
2, 3: e_1: R^1 = Ph, R^2 = H; **e_2**: $R^{1'}$ = Ph/H, $R^{2'}$ = H/Ph; **e_3**: $R^{1'}$ = H, $R^{2'}$ = Ph

Scheme 1 Synthesis of disubstituted dithioether dithiols **3a**.

RESULTS AND DISCUSSION

In our first attempts to study the reactivity of β,β'-dihydroxydithioethers **2a–e**, we tried to prepare the corresponding tosylates according to standard protocols[30,31] in order to synthesize the dithiols containing six sulfur atoms by condensation of dimercaptoethane with these tosylates. In all cases, no tosylation reaction was observed and the starting compounds were recovered unchanged. This is presumably due to the existence of an adjacent sulfur atom. Consequently, a direct thiolation of the two hydroxyl groups was attempted. According to the literature,[1,32] the condensation of alcohols in concentrated hydrochloric acid with thiourea followed by hydrolysis of the thiouronium salt intermediate under basic conditions is considered to be a good thiolation method, which is widely used for the preparation of primary and secondary thiols. Therefore, the new symmetric disubstituted dithioetherdithiols **3a–e** have been prepared in this way. In the case of styrene oxide, we

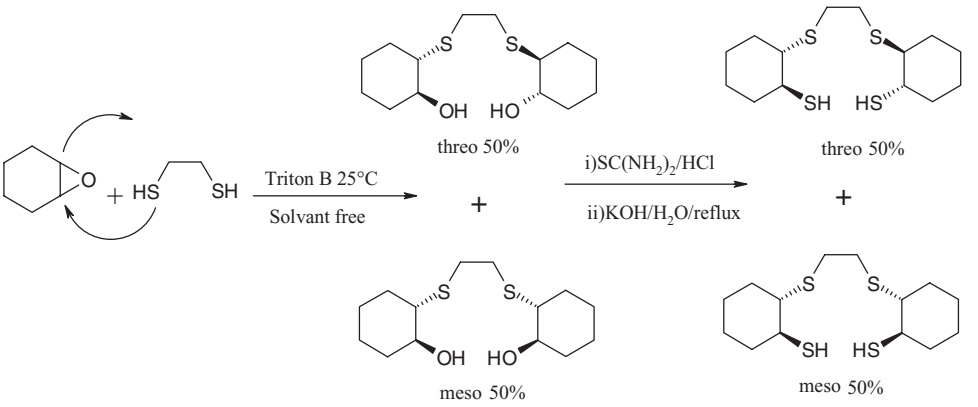
Table 1 Symmetric disubstituted dithioethers dithiols

Epoxide 1	Thioetherdiols 2	Thioetherdithiols[a] 3	Yield (%)	bp (°C/0.01 mmHg)
 **1a**	 **2a**	 **3a**	87	87
 **1b**	 **2b**	 **3b**	85	134
 **1c**	 **2c**	 **3c**	70	oil
 **1d**	 **2d**	 **3d**	70	oil
 **1e**	 **2e$_1$** 52%	 **3e$_1$** 53%	70[b]	176[c]
	 **2e$_2$** 31%	 **3e$_2$** 32%		
	 **2e$_3$** 17%	 **3e$_3$** 15%		

[a]The ratio of the three isomers was determined by ^{1}H NMR. [b]Total yield of three isomers. [c]The mixture of isomeric products was purified by distillation.

showed in a previous letter[27] that the ring opening of this epoxide with dimercaptoethane using benzyltrimethylammonium hydroxide (Triton B) as catalyst led to a mixture of three regioisomers of $\beta,'$-dihydroxydithioethers **2e$_1$**–**e$_3$** (Table 1). The three isomers were converted into their homologous thioether thiols **3e$_1$**–**e$_3$** and the mixture of isomers was purified by distillation. The ratio of the three isomers was determined by ^{1}H spectroscopy. Compounds **3a**, **3b**, **3d**, and **3e** should be obtained as mixtures of diastereomers. However, since the two stereogenic centers within the molecule are far from each other, the diastereoisomers could not be discerned by NMR techniques as in the case of their precursors **2a**, **2b**, **2d**, and **2e**.[27] The ^{1}H NMR spectrum shows a sharp singlet for the two methylene groups

of the dimercaptoethane moiety ($-SCH_2-CH_2S-$) at around $\delta = 2.80$ ppm. As the compounds **3a**, **3b**, and **3d** are symmetric, the ^{13}C NMR spectra show the existence of only three different signals corresponding to the three aliphatic carbon atoms of one isomer, besides the peaks related to the carbon atoms of the alkyl groups. In addition of the peaks related to the aromatic carbon atoms, six distinct signals were observed in the ^{13}C NMR spectrum of the mixture of $\mathbf{3e_1}$, $\mathbf{3e_2}$, and $\mathbf{3e_3}$. This is not the case for the cyclohexane derivative **3c**, for which two singlets of the same intensity were observed for these methylene groups at $\delta = 2.80$ ppm and at $\delta = 2.83$ ppm. The existence of two diastereomers for the cyclohexane derivative was shown in our previous work.[27] This may be explained if we assume that the cyclohexene oxide **1c** gave exclusively *trans*-products **2c**,[33] formed as an equimolar mixture of the *meso*- and *threo*-isomers which are transformed into the homologous *meso*- and *threo*-isomers **3c** too (Scheme 2). Examination of the ^{13}C NMR spectra of **3c** showed doubling of a number of the peaks. ^1H NMR spectra of **3c** exhibited correct integrals but it showed two signals for the CH_2S group. The isomeric ratio is determined from CH_2S signals intensity.



Scheme 2 Formation of stereoisomers of **3c**.

It should be noted that in all cases variable amounts of the corresponding disulfide and trisulfide compounds (dimers and trimers) were formed by air oxidation of the aqueous thiolates. The formation of compounds **3a–e** was confirmed by ^1H and ^{13}C NMR spectroscopy and HRMS. In all cases, the ^1H NMR spectra showed the absence of a singlet around δ 3.77 ppm due to the two (OH) protons and the presence of a multiplet between δ 1.70 and 1.80 ppm assigned to the protons of SH groups. The ^{13}C NMR spectra display characteristic signals of all carbons.

As compounds **3** are expected to be excellent chelating agents toward soft metal ions, we used **3b** as a ligand to prepare gold nanoparticles (AuNPs) due to the soft character of both Au and S.[34,35] These AuNPs could have applications in biological fields and catalytic reactivity. The preparation was carried out in aqueous solution using tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$) as precursor and sodium borohydride ($NaBH_4$) as a reducing agent with the ligand **3b** in a molar ratio of Au:ligand = 600:1. Tetrachloroauric acid and the ligand **3b** were first mixed in water to promote the formation of metal-ligand precursors. The precursor formation showed a rapid color change of the originally yellow solution to colorless. Addition of $NaBH_4$ initiates reduction of the Au ions and rapid growth of the Au nanocrystals.

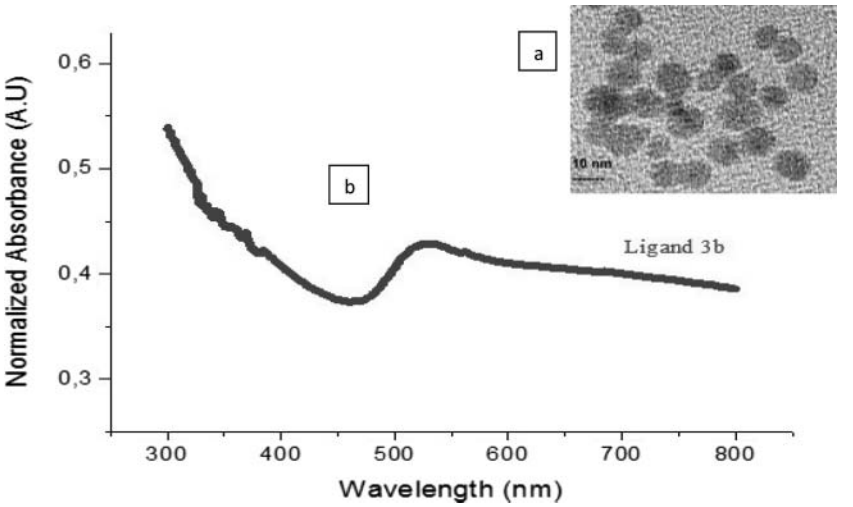


Figure 1 TEM images (a) and UV-Vis spectrum (b) of AuNPs of **3b**.

The AuNPs were characterized by transmission electron microscopy (TEM) and UV-vis absorption spectroscopy. The results are shown in Figure 1.

The TEM image shows the formation of a clear distribution of colloidal nanoparticles formed between gold atoms and the ligand **3b**. This image does not show any nanocrystal clumping, and also shows that the AuNPs exhibit a spherical shape with a diameter of 10 nm. The UV-Vis spectroscopy result is in good agreement with the TEM image and reveals that AuNPs have a maximum absorption band at 530 nm which indicates the formation of AuNPs with a size of 10 nm. These nanoparticles appear to exhibit good stability. Indeed, the peak characteristic of AuNPs absorbance shows no shift after several months of synthesis. In addition, no change in color of the solution is observed.

Compared to other ligands as PEG-SH[25] used in the complexation of gold, the ligand **3b** is highly stable even though it has a short chain. Furthermore, the two SH functions of **3b** increase the stability of the AuNPs.

The importance of the synthesis of colloidal solutions with thiols mainly rests on biological applications. In fact, working in this area under extreme conditions of pH, which involves particles with good stability, the use of thiols have the greatest gold affinity.

In summary, we have achieved the conversion of β,β'-dihydroxydithioethers **2a–e** into their corresponding disubstituted dithioethers dithiols **3a–e** in good yields. To our knowledge, these compounds, except the product **3a**[36] have not been reported previously and may be useful intermediates for the synthesis of lipophilic thiacrown ethers. We have also demonstrated that compounds **3** can be used for the preparation of colloidal gold solution in aqueous phase using $HAuCl_4 \cdot 3H_2O$. These colloidal solutions exhibit remarkable stability.

EXPERIMENTAL

^{1}H and ^{13}C NMR, UV-Vis Spectroscopy, and Transmission Electron Microscopy

The ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ as solvent on a Bruker AC 300 spectrometer. The chemical shifts are reported in ppm relative to TMS (internal reference). For the ^{1}H NMR, the multiplicities of signals are indicated by the

following abbreviations: s: singlet, d: doublet, t: triplet, m: multiplet. Coupling constants J are given in Hz. HRMS spectra were obtained by use of a MAT 95 SBE instrument. TEM measurements were made on a JEOL 2011 microscope operating at 100 kV. This microscope is equipped with a Gatan Imaging Filter 2000 so as to conduct an electron energy-loss spectroscopy (EELS) analysis. Such an analysis is a powerful technique to provide a cartographic picture of the distribution of chemical elements in the observed nanoparticles. The absorption spectra were obtained with a PERKIN ELMER UV/VIS spectrometer lambda11.

Preparation of Dithiols

To a stirred solution of thiourea (2.51 g, 33 mmol) in 8 mL of conc. aqu. HCl, were added the thioetherdiol **2** (15 mmol) at room temperature. The mixture was refluxed for 9 h. The resulting solution was then cooled in an ice bath and 5.65 g (0.101 mol) of KOH in 35 mL of H_2O were cautiously added. This mixture was refluxed for 3 h. Then, the resulting solution was allowed to cool, acidified with 10% aqu. HCl to pH = 2–3, and extracted with diethyl ether (3 Î 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by distillation except the product **3d** which was isolated by column chromatography (silica gel $60F_{254}$, heptane /EtOAc 80:20).

Preparation of AuNPs

AuNPs were prepared following literature methods[25]: an amount of 156 μL of 50.8 mM $HAuCl_4{\cdot}3H_2O$ solution and the desired molar concentration of **3b**-ligand were dissolved in 25 mL of deionized H_2O; the mixture was then stirred for 1 h. An amount of 72 μL of 880 mM $NaBH_4$ stock solution in deionized H_2O was added (in aliquots of 18 μL) over 30 min with vigorous stirring. The mixture was then left under stirring for at least 3 h. In our experimental protocol, we used 10 times total molar excess of the reducing agent during the growth and passivation steps, i.e., a total $NaBH_4$:Au molar ratio ~10.

4,7-Dithiadecane-2,9-dithiol (3a). Yield = 87%. ^{1}H NMR: 1.36 (d, 6H, J = 6, $2CH_3$); 1.74 (m, 2H, 2SH); 2.55–2.78 (m, 4H, CH_2S); 2.81 (S, 4H, SCH_2CH_2S); 2.92–3.09 (m, 2H, CHSH). ^{13}C NMR: 20.0 (CH_3); 31.87 (C, SCH_2CH_2S); 38.67(CH_2); 43.62 (CHSH). HRMS: calcd. 265.0189 for $C_8H_{18}S_4Na$, found 265.0193 $(M+Na)^+$.

5,8-Dithiadodecane-3,10-dithiol (3b). Yield = 85%. ^{1}H NMR: 0.99 (t, 6H, CH_3); 1.54 (m, 4H, CH_2); 1.80 (m, 2H, SH); 2.70 (m, 4H, CH_2S); 2.75 (s, 4H, SCH_2CH_2S); 2.89 (m, 2H, CHSH). ^{13}C NMR: 11.23 (CH_3); 29.48 (CH_2CH_3); 31.14 (SCH_2CH_2S); 42.36 (CH_2S); 43.49 (CHSH). HRMS: calcd. 293.0502 for $C_{10}H_{22}NaS_4$, found 293.0508 $(M+Na)^+$.

2,2′-[Ethane-1,2-diylbis(sulfanediyl)]dicyclohexanethiol (3c). Yield = 72%. ^{1}H NMR: 1.27–1.41 [m, 8H, $(CH_2)_2$]; 1.50–1.90 [m, 8H, $(CH_2)_2$]; 1.77 (m, 2H, SH); 2.42 (m, 2H, CH), 2.70–2.75 (m, 2H, CH), 2.80, 2.83 (two singlets, 4H, SCH_2CH_2). ^{13}C NMR: 24.10, 24.30 (two peaks, CH_2); 24.02, 25.90 (two peaks, CH_2); 31.09, 31.77 (two peaks, CH_2); 32.45, 32.92 (two peaks, SCH_2CH_2S); 33.42, 33.78 (two peaks, CH_2); 46.30, 46.70 (two peaks, CH); 48.32, 48.90 (two peaks, CHSH). HRMS: calcd. 345.0815 for $C_{14}H_{26}NaS_4$, found 345.0811 $(M+Na)^+$.

1,10-Diphenoxy-4,7-dithiadecane-2,9-dithiol (3d). Yield = 70%, Yellow oil. ^{1}H NMR: 1.85 (m, 2H, SH); 2.58–2.83 (m, 4H, CH_2S); 2.81 (s, 4H, SCH_2CH_2S); 3.35 (m, 2H, CH); 4.02–4.30 (m, 4H, CH_2O); 6.80–7.40 (m, 10H, H_{ar}). ^{13}C NMR: 32.91 (SCH_2CH_2S);

35.42 (CH_2S); 57.10 (CH); 70.30 (CH_2O); 114.92–159.38 (C_{ar}). HRMS: calcd. 449.0713 for $C_{20}H_{26}O_2SNa$, found 449.0715 $(M+Na)^+$.

1,8-Diphenyl-3,6-dithiaoctane-1,8-dithiol ($3e_1$), 2,7-Diphenyl-3,6-dithiaoctane-1,8-dithiol ($3e_2$) and **2,7-Diphenyl-3,6-dithiaoctane-1,8-dithiol ($3e_3$)**. Total yield = 70%. **1,8-Diphenyl-3,6-dithiaoctane-1,8-dithiol ($3e_1$)**. ^1H NMR: 1.50–1.70 (m, 2H, SH); 2.80 (s, 4H, SCH_2CH_2S); 2.75–3.10 (m, 4H, CH_2S); 3.95 (m, 2H, CH); 6.90–7.50 (m, 10H, H_{ar}). ^{13}C NMR: 33.56 (SCH_2CH_2S); 41.90 (CHPh); 43.46 (CH_2S); 127.14–141.77 (C_{ar}). HRMS: calcd. 389.0502 for $C_{18}H_{22}NaS_4$, found 389.0505 $(M+Na)^+$.—**2,7-Diphenyl-3,6-dithiaoctane-1,8-dithiol ($3e_2$)**. ^1H NMR: 1.50–1.70 (m, 2H, SH); 2.80 (s, 4H, SCH_2CH_2S); 3.10–3.40 (m, 4H, CH_2S); 4.15 (m, 2H, CH); 6.90–7.50 (m, 10H, H_{ar}). ^{13}C NMR: 31.34 (SCH_2CH_2S); 35.15 (CH_2SH); 48.77 (CHPh); 127.14–139.99 (C_{ar}). HRMS: calcd. 389.0502 for $C_{18}H_{22}NaS_4$, found 389.0505 $(M+Na)^+$.—**2,7-Diphenyl-3,6-dithiaoctane-1,8-dithiol ($3e_3$)**. ^1H NMR: 1.50–1.70 (m, 2H, SH); 2.81 (s, 4H, SCH_2CH_2S); 2.90–3.15 (m, 2H, CH_2SH); 3.10–3.35 (m, 2H, SCH_2CH); 4.12 (m, 2H, CHPh); 6.90–7.50 (m, 10H, H_{ar}). ^{13}C NMR: 31.34 (CH_2SC-Ph); 33.56 (SCH); 35.15 (CH_2SH); 41.90 (HSCHPh), 43.46 (CH_2CHPh), 48.77 (SCHPh), 127.14–141.77 (C_{ar}). HRMS: calcd. 389.0502 for $C_{18}H_{22}NaS_4$, found 389.0505 $(M+Na)^+$.

REFERENCES

1. William, R.; Daryle, H. B. *J. Am. Chem. Soc.* **1969,** 91, 4694-4697.
2. Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981,** 46, 4481-4485.
3. Bush, R. P. *Platinum Metals Rev*. **1991,** 35, 202-208.
4. Edema, J. J. H.; Buter, J.; Kellog, R. M. *Tetrahedron* **1994,** 50, 2095-2098.
5. Metzke, M.; Guan, Z. *Biomacromolecules* **2008,** 9, 208-215.
6. Hedfors, C.; Ostmark, E.; Malmstrom, E.; Hult, K.; Martinelle, M. *Macromolecules* **2005,** 38, 647-649.
7. Kuroda, H.; Tomita, I.; Endo, T. *Polymer* **1997,** 38, 6049-6054.
8. Meng, Y. Z.; Liang, Z. A.; Lu, Y. X.; Hay, A. S. *Polymer* **2005,** 46, 11117-111124.
9. Ito, M.; Koyakumanu, K.; Ohta T.; Takaya, H. *Synthesis* **1995,** 376-378.
10. Tortora, M.; Cacalieri, F.; Chiessi, E.; Paradossi, G. *Biomacromolecules* **2007,** 8, 209-214.
11. Quik, D. J.; Anseth, K. S. *Pharm. Res.* **2003,** 20, 1730-1737.
12. Nuttelman, C. R.; Tripodi, M. C.; Anseth, K. S. *Biomaterials* **2002,** 23, 3617-3626.
13. Nguyen, K. T.; West, J. L. *Biomaterials* **2002,** 23, 4307-4314.
14. Firouzabadi, H.; Iranpoor, N.; Jafarpour, M. *Tetrahedron Lett*. **2006,** 47, 93-97.
15. Nikac, M.; Brimble, M. A.; Crumbie, R. L. *Tetrahedron* **2007,** 63, 5220-5226.
16. Houcine, Z.; Romdhani-Younes, M.; Chaabouni, M. M.; Baklouti, A. *Tetrahedron Lett*. **2011,** 52, 881-883.
17. Bourlès, E.; Sousa, R. A. D.; Galardon, E.; Selkti, M.; Tomas, A.; Artand, I. *Tetrahedron* **2007,** 63, 2466-2471.
18. Santos, L. L.; Ruiz, V. R.; Sabater, M. J.; Corma, A. *Tetrahedron* **2008,** 64, 7902-7909.
19. Loeb, S. J.; Shimizu, G. K. *J. Chem. Soc. Chem. Commun.* **1991,** 1119-1121.
20. Ganesh, V.; Pal, S. K.; Kumar, S.; Lakshminarayanan, V. *J. Colloid Interface Sci.* **2006,** 296, 195-203.
21. Ulman, A. *Chem. Rev.* **1996,** 96, 1533-1554.
22. Xiao, Y.; Patolsky, F.; Katz, E.; Hainfeld, J. F.; Willner, I. *Science* **2003,** 299, 1877-1881.
23. de Boer, B.; Meng, H.; Perepichka, D. F.; Zheng, J.; Frank, M. M.; Chabal, Y. J.; Bao, Z. N. *Langmuir* **2003,** 19, 4272-4284.
24. Aslam, M.; Chaki, N. K.; Sharma J.; Vijayamohanan, K. *Curr. Appl. Phys.* **2003,** 3, 115-127.
25. Eunkeu, O.; Kimihiro, S.; Ramasis, G.; Hedi, M. *Langmuir* **2010,** 26, 7604-7613.

26. Romdhani-Younes, M.; Chaabouni, M. M. *Synth. Commun.* **1999,** 29, 3939-3948.
27. Romdhani-Younes, M.; Chaabouni, M. M.; Baklouti, A. *Tetrahedron Lett*. **2001,** 42, 3167-3169.
28. Romdhani-Younes, M.; Chaabouni, M. M.; Baklouti, A. *Tetrahedron Lett*. **2003,** 44, 5263-5265.
29. Houcine, Z.; Chehidi, I.; Romdhani-Younes, M.; Chaabouni, M. M.; Baklouti, A. *Tetrahedron Lett.* **2007,** 48, 5645-5647.
30. Comagic, S.; Schirrmacher, R. *Synthesis* **2004,** 885-888.
31. Yan, J.; Li, J.; Cheng, D. *Synlett* **2007,** 2442-2444.
32. Yatsimirskii, K. B.; Pavlishchuk, V. V.; Strizhak, P. E. *J. Gen. Chem. USSR (Engl. Transl).* **1987,** 57, 2750-2755.
33. De Sousa, A. S.; Hancock, R. O. *J. Chem. Soc. Chem.Commun.* **1995,** 415-416.
34. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. *J. Chem. Soc. Chem. Commun.* **1994,** 801-802.
35. Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. *J. Chem. Soc. Chem. Commun.* **1995,** 1655-1656.
36. Adams, E. P.; Doyle, F. P.; Hatt, D. L.; Holland, D. O.; Hunter, W. H.; Mansford, K. R. L.; Nayler, J. H. C.; Queen, A. *J. Chem. Soc.* **1960,** 2649-2659.