Chinese Chemical Letters 24 (2013) 909–911

Contents lists available at SciVerse ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Synthesis of 3,3,5,5-tetrabenzyl-1,2,4-trithiol and 1,2-dis(1,3-arylpropan-2-yl)disulfane

Fu Feng, Meng Huang, Zheng-Chao Duan, Wei-Bing Hu *

School of Chemistry and Environmental Engineering, Hubei Institute for Nationalities, Enshi 445000, China

ARTICLE INFO

Article history:
Received 4 March 2013
Received in revised form 28 April 2013
Accepted 8 May 2013

Keywords:
1,3-Diphenyl-2-propanone
Synthesis
Sulfur-containing compounds

ABSTRACT

Novel sulfur-containing compounds (**3a**–**3c**, **4a**–**4c**) were obtained in ethanol with 1,3-diphenyl-2-propanone as the starting material. The advantages of this procedure were mild reaction conditions, simple protocol, and high yields. The structures of the products were characterized by IR, ^{1}H NMR, MS and elementary analysis. The crystal of the new compound **4a** belongs to monoclinic, space group C2 with $a = 18.727(3)$, $b = 6.5179(9)$, $c = 13.7576(18)$ Å, $\beta = 131.0610(10)^\circ$, $V = 1266.2(3)$Å^3, $Z = 2$, $Dc = 2.136$ g/cm^3, $\mu = 1.078$ mm^{-1}, $F(0\,0\,0) = 843$, $R = 0.0490$ and $wR = 0.1247$ for 3211 observed reflection with $I > 2\sigma(I)$. X-ray analysis reveals that the molecule is not symmetrical, the molecular structure is stabilized by weak π–π stacking interactions, and no classical hydrogen bonds can be observed.

1. Introduction

Mercapto-compounds are important intermediates in organic synthesis, dye, and are widely used for the synthesis of medicines, polymeric materials, aluminum alloy corrosion inhibitors and analytical reagents for heavy metal ion complexation [1,2]. Moreover, sulfur-containing compounds are widely used spices in food flavor and play an important role in improving the quality and grade of flavors [3,4]. So, a great number of studies have appeared on sulfur-containing compounds [5]. In this paper, we first synthesized 1,3-diphenylpropane-2,2-dithiol using 1,3-diphenyl-2-propanone as the starting material. Several related novel compounds (**3a**–**3c**, **4a**–**4c**) were then also synthesized. The procedures required only mild reaction conditions and simple protocols but gave high yields. The crystal structure of compound **4a** was determined by X-ray diffraction. The synthetic route to produce compounds **3**–**4** is shown in Scheme 1.

2. Experimental

Infrared spectra were measured on a Nicolet 360 FT-IR instrument using KBr pellet in the 4000–400 cm^{-1} range. ^{1}H-NMR spectra were collected on a Mercury Plus-400 MHz spectrometer in DMSO-d_6 solution with TMS as an internal standard. Elemental analysis was performed by a Vario EL III elementary analysis instrument. Melting point was measured on a XT4A melting-point apparatus with microscope and uncorrected. Single crystal X-ray diffraction data were collected on a BRUCKER SMART APEX-CCD diffractometer equipped with a graphite-monochromatic Mo K_α radiation ($\lambda = 0.71073$ Å). 1,3-Diphenyl-2-propanone and other chemicals were purchased from commercial sources.

2.1. Synthesis of compounds 3a–3c

A solution of 0.01 mol of iodine in 50 mL of benzene was added, with stirring, to 0.01 mol of 1,3-diarylpropane-2,2-dithiol (**2**) in 100 mL of benzene in an ice bath. The first portion of the iodine was rapidly decolorized, but the color soon persisted. The flask was allowed to warm to room temperature and stirring continued for 2 days. The unchanged iodine was then destroyed by washing the benzene solution with aqueous sodium bisulfite. The pale yellow benzene layer was washed with saturated sodium chloride solution. Evaporation of the benzene at reduced pressure gave a reddish semisolid, which was extracted with hot *n*-hexane. The crude material was recrystallized from *n*-hexane-chloroform to give pure products **3a**–**3c**.

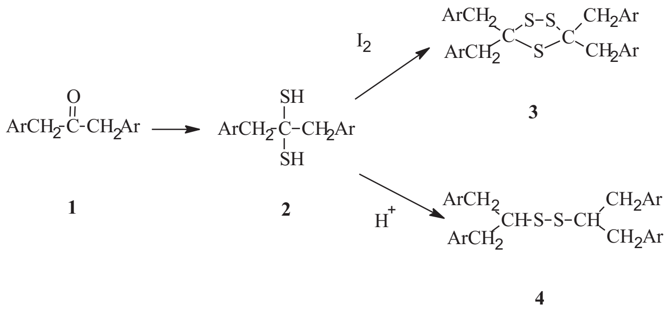
3,3,5,5-Tetrabenzyl-1,2,4-trithiole (**3a**): White solid, yield 83%, mp 144–146 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.79(s, 8H, CH$_2$), 7.31–7.37 (m, 12H, Ar-H), 7.43–7.48 (m, 8H, Ar-H); IR (KBr, cm^{-1}): υ 3032, 2917, 1611, 1593; EI-MS (m/z): 91 (100%), 484 (M$^+$, 4.29%). Anal. Calcd. for $C_{30}H_{28}S_3$: C 73.38, H 5.79; Found: C 73.52, H 5.71.

3,3,5,5-Tetra(4-bromobenzyl)-1,2,4-trithiole (**3b**): White solid, yield 77%, mp 173–175 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.80 (s, 8H, CH$_2$), 7.33–7.37 (m, 8H, Ar-H), 7.59–7.64 (m, 8H, Ar-H); IR (KBr,

---

* Corresponding author.
E-mail address: fengfu04971118@163.com (W.-B. Hu).

1001-8417/$ – see front matter © 2013 Wei-Bing Hu. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.
http://dx.doi.org/10.1016/j.cclet.2013.05.041



3a: Ar=C_6H_5; **3b**: Ar=4-BrC_6H_4; **3c**: Ar= 4-$NO_2C_6H_4$
4a: Ar=C_6H_5; **4b**: Ar=4-BrC_6H_4; **4c**: Ar= 4-$NO_2C_6H_4$

Scheme 1. Synthetic route of compounds **3a–3c** and **4a–4c**.

cm^{-1}): υ 3025, 2917, 1607, 1591; EI-MS (m/z): 169 (100%), 796 (M$^+$, 1.45%). Anal. Calcd. for $C_{30}H_{24}Br_4S_3$: C 45.23, H 3.02; Found: C 45.37, H 3.11.

3,3,5,5-Tetra(4-nitrobenzyl)-1,2,4-trithiole (**3c**): White solid, yield 73%, mp 201–203 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.90 (s, 8H, CH_2), 7.37–7.40 (m, 8H, Ar-H), 8.21–8.25 (m, 8H, Ar-H); (KBr, cm^{-1}): υ 3047, 2911, 1611, 1597; EI-MS (m/z): 136 (100%), 664 (M$^+$, 3.46%). Anal. Calcd. for $C_{30}H_{24}N_4O_8S_3$: C 54.22, H 3.61, N 8.43; Found: C 54.41, H 3.54, N 8.59.

*2.2. Synthesis of compounds **4a–4c***

A solution of 1,3-diarylpropane-2,2-dithiol (0.01 mol) in 50 mL of absolute alcohol was saturated with hydrogen chloride at 0–5 °C, and the mixture was stirred at 78 °C. After 1.5 h, the flask was stored in a refrigerator overnight and a white solid appeared. The crude product was recrystallized from ethanol to give pure products **4a–4c**.

An alcohol solution of compound **4a** was allowed to stand at room temperature and the alcohol was allowed to slowly evaporate. White crystals suitable for X-ray diffraction analysis were isolated one week later.

1,2-Dis(1,3-diphenylpropan-2-yl)disulfane (**4a**): white solid, yield 90%, mp 126–128 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.75 (d, J = 7.2 Hz, 8H, CH_2), 3.28–3.31 (m, 2H, CH), 7.26–7.29 (m, 12H, Ar-H), 7.41–7.45 (m, 8H, Ar-H); IR (KBr, cm^{-1}): υ 3019, 2917, 1593; EI-MS (m/z): 91 (100%), 454 (M $^+$, 3.19%). Anal. Calcd. for $C_{30}H_{30}S_2$: C 79.30; H 6.61. Found: C 79.58, H 6.43.

1,2-Dis[1,3-di(4-bromophenylpropan)-2-yl]disulfane (**4b**): White solid, yield 81%, mp 143–145 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.76 (d, J = 7.2 Hz, 8H, CH_2), 3.27–3.29 (m, 2H, CH), 7.31–7.34 (m, 8H, Ar-H), 7.57–7.61 (m, 8H, Ar-H); IR (KBr, cm^{-1}): υ 3021, 2911, 1597; EI-MS (m/z): 169 (100%),766 (M $^+$, 1.02%). Anal. Calcd. for $C_{30}H_{26}Br_4S_2$: C 47.00, H 3.39; Found: C 47.12, H 3.47.

1,2-Dis[1,3-di(4-nitrophenylpropan)-2-yl]disulfane (**4c**): White solid, yield 83%, mp 197–199 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.91 (d, J = 7.2 Hz, 8H, CH_2), 3.35 (m, 2H, CH), 7.38 (m, 8H, Ar-H), 8.19 (m, 8H, Ar-H); (KBr, cm^{-1}): υ 3021, 2907, 1599; EI-MS (m/z): 136 (100%), 634 (M $^+$, 5.71%). Anal. Calcd. for $C_{30}H_{26}N_4O_8S_2$: C 56.78, H 4.10, N 8.83; Found: C 56.93, H 4.02, N 8.76.

3. Results and discussion

The synthesis of compound **2** followed literature procedures [6] and the isolated yield was in agreement with the literature report.

The ^{1}H NMR, IR and elemental analysis data of these products supported their proposed chemical structures. A white single crystal of compound **4a** with dimensions of 0.16 mm × 0.15 mm × 0.10 mm was chosen for X-ray diffraction analysis performed on a BRUCKER SMART APEX-CCD diffractometer equipped with a graphite-monochromatic Mo K_α radiation (λ = 0.71073 Å) radiation at 298(2) K. A total of 5119 reflections were collected in the range of $1.96° < \theta < 30.00°$ by using a ψ–ω scan mode with 3278 independent ones (R_{int} = 0.0464), in which 3211 with $I > 2\sigma(I)$ were observed and were used in the subsequent refinements. The data set was corrected by SADABS program, the structure was solved by direct methods and expanded by Difference Fourier techniques with SHELXS-97 [7]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were added according to the theoretical models.

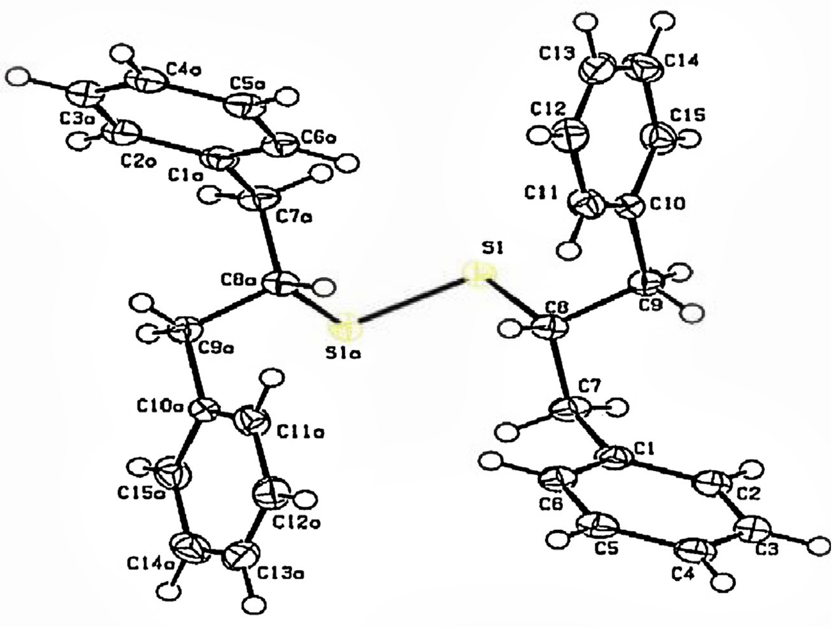


Fig. 1. Molecular structure of compound **4a**.

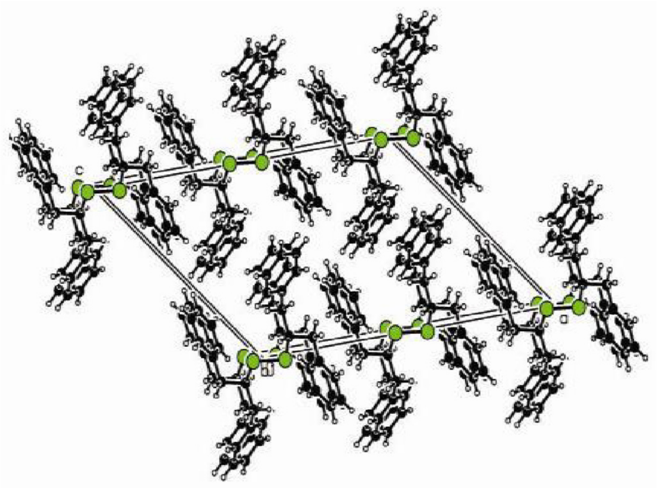


Fig. 2. Packing diagram of compound **4a**.

The structure was refined by the full-matrix least-squares method on F^2 with SHELXL-97 [8]. The final refinement gave $R = 0.0490$, $wR = 0.1247$ ($w = 1/[\sigma^2(F_o^2)+(0.0682P)^2+1.7325P]$, where $P = (FO^2+2FC^2)/3$, $S = 1.059$,$(\Delta/\sigma)_{\max} = 0.001$, $(\Delta\rho)_{\max} = 2.403$ and $(\Delta\rho)\ \min = -0.296/\text{Å}^3$.

The molecular structure and packing diagram are depicted in Figs. 1 and 2, respectively. In the crystal structure, the bond length (1.834(2)) of C(8)-S(1) is longer than that (1.533(3)) of C(7)-C(8) and the bond length of S(1)-S(1a)(2.0284(9)) is the longest. Moreover, there is no center of symmetry and symmetry plane in the molecule. So the molecule is not symmetrical. In the aromatic rings in the molecule, the molecular dimensions are as expected with the aromatic C–C bond distances between 1.388(4) and 1.408(4) Å, and these bond lengths are even. The aromatic C–C–C bond angles ranging from 118.1(2) to 121.14(18)° are almost within the normal ranges [9]. Each of the rings is nearly planar. It can be seen that the molecular structure is stabilized by weak π–π stacking interactions and there no classical hydrogen bonds can be observed.

4. Conclusion

In conclusion, a series of novel sulfur-containing compounds were synthesized in ethanol using 1,3-diphenyl-2-propanone as the starting material. The advantages of this procedure include mild reaction conditions, simple protocols, and high yields. The crystal structure of the new compound **4a** was obtained. Other properties of these compounds are being studied.

Acknowledgments

We are grateful for the Natural Science Foundation of Hubei Province (No. 2012FFB01103), the Hubei Provincial Department of Education (No. Q20131905), the National Natural Science Foundation of China (No. 21262011), and the Fund of Ethnic Affairs Commission of China (No. 12HBZ010).

References

[1] J.M. Khurana, K.S. Prabhat, Chemoselective alkylation of thiols: a detailed investingation of reactions of thiols with halides, Synth. Commun. 22 (1992) 1691–1702.
[2] E.S. Paul, Inorganic halide salt catalysts for hydroxyalkylation of phenols or thiophenols, US 4341905, 1982.
[3] I. Katz, W.J. Evers, A.S. Highlands, Flavoring compositions and processesutilizing alpha-ketothiols, US 3773524, 1973.
[4] W.J. Evers, H.H. Heinsohn, F.L. Schmitt, alpha-Oxy(oxo)mercaptan perfume and cologne compositions, US 4070308, 1978.
[5] D. Craig, K. Daniels, Additive pummerer reactions of vinylic sulphoxides. Synthesis of 2-(phenylsulphenyl) aldehydes and primary alcohols, Tetrahedron Lett. 32 (1991) 6973–6976.
[6] F. Feng, W.B. Hu, H.X. Liu, Study on synthesis of 1, 3-diphenyl-2,2-dithiol, J. Hubei Inst. Nationalities 24 (2006) 69–70.
[7] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, 1990.
[8] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, 1997.
[9] F. Feng, Solvent-free Michael addition reaction of fluorene with chalcon, Chin. Chem. Lett. 22 (2011) 29–32.