Synthesis of Thieno[3,4-*c*]thiophene Derivatives Bearing *tert*-Butylthio and Aryl Substituents

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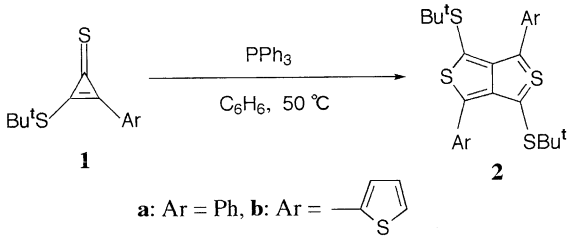
1,4-Bis(*tert*-butylthio)-3, 6-diphenylthieno[3, 4-*c*]thiophene (**2a**) and 1,4-bis(*tert*-butylthio)-3,6-di(2-thienyl)thieno[3,4-*c*]-thiophene (**2b**) were synthesized from 2-*tert*-butylthio-3-phenylcyclopropenethione (**1a**) and 2-*tert*-butylthio-3-(2-thienyl)cyclopropenethione (**1b**), respectively, by treatment with triphenylphosphine in benzene.

Although thieno[3,4-*c*]thiophenes are of interest as 10π-electron heterocycles with a nonclassical structure, only a few thieno[3,4-*c*]thiophenes are known.[1] Previously, our laboratory has developed a convenient synthetic method for the preparation of 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]thiophenes from bis(alkylthio)cyclopropenethiones using triphenylphosphine or tributylphosphine.[2] However, it was impossible to prepare the thieno[3,4-*c*]thiophene system from 2,3-diarylcyclopropenethione by this method, because of the formation of 2,3,5,6-tetraarylthieno[3,2-*b*]thiophene.[3] This result led us to investigate whether two alkylthio groups are essential for the formation of the thieno[3,4-*c*]thiophene system or not. We now report our findings that 2-*tert*-butylthio-3-phenylcyclopropenethione (**1a**)[4] and 2-*tert*-butylthio-3-(2-thienyl)cyclopropenethione (**1b**),[5] bearing a *tert*-butylthio group, can be converted into 1,4-bis(*tert*-butylthio)-3,6-diphenylthieno[3,4-*c*]-thiophene (**2a**) and 1,4-bis(*tert*-butylthio)-3,6-di(2-thienyl)-thieno[3,4-*c*]thiophene (**2b**), respectively, by our method, as shown in Scheme 1.



Scheme 1.

To a solution of **1a** or **1b** in dry benzene was added a solution of triphenylphosphine (0.6 equiv.) in dry benzene under argon atmosphere and the mixture was stirred at 50 °C for 20 h. After the reaction, the solvent was evaporated under reduced pressure. Chromatography on silica-gel with dichloromethane-hexane (1 : 9) as eluent gave **2a**[6] and **2b**[7] in 30 and 21% yields, respectively. In this reaction, the use of triphenylamine instead of phosphines did not afford any **2a**,**b**, but gave back the starting materials. The structure of **2a** was determined by an X-ray crystal structure analysis. The ORTEP drawing of **2a** is shown in Figure 1.[8] Thus, it was established that the *tert*-butylthio and phenyl groups are attached in 1,4- and 3,6-positions, respectively, and that the thieno[3,4-*c*]thiophene framework is

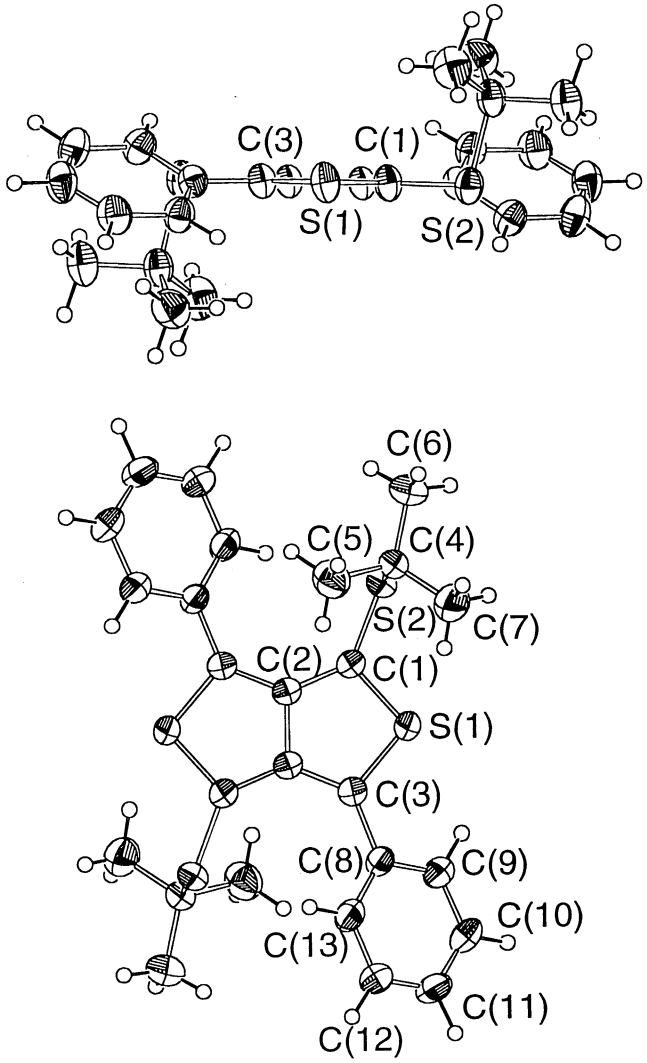


Figure 1. ORTEP[9] drawing and atomic numbering of **2a**, viewed perpendicular and parallel to the thieno[3,4-*c*]thiophene ring. Selected structural parameters, S(1)-C(1) 1.708 (3), C(1)-C(2) 1.411 (4), C(2)-C(2^i) 1.489(6), C(2^i)-C(3) 1.418(4), S(2)-C(1) 1.763 (3), S(2)-C(4) 1.875 (3), C(3)-C(8) 1.492 (4), C(8)-C(9) 1.395 (4) Å. C(1)-S(1)-C(3) 97.4(1), S(1)-C(1)-C(2) 109.3(2), C(1)-C(2)-C(2^i) 112.0 (2), S(1)-C(1)-S(2) 117.3(2), C(1)-S(2)-C(4) 103.4(1), C(8)-C(3)-C(2^i) 133.7(3), C(8)-C(13)-C(12) 121.4 (3), C(11)-C(12)-C(13) 119.5 (3)°.
Symmetry code i: -x, -y, -z.

planar and the plane of the phenyl group is not coplanar to the thieno[3,4-*c*]thiophene ring. The results of the IR, ^{1}H, and ^{13}C NMR spectra and the elemental analyses of **2a**,**b** were

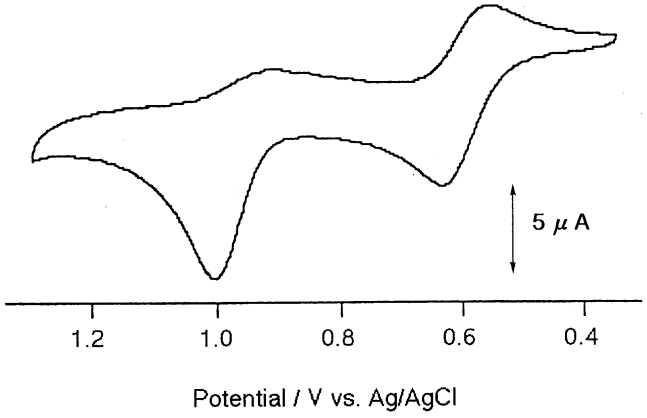


Figure 2. Cyclic voltammogram of **2a**. Scan rate: 0.05 V/sec.

consistent with the assignment of their structures. The UV-VIS spectra of **2a**,**b** in hexane exhibited intense absorption peaks at 516 and 538 nm, respectively, which were shifted to longer wavelength by 10 and 32 nm, respectively, as compared with that of 1,3,4,6-tetrakis(*tert*-butylthio)thieno[3,4-*c*]thiophene reported previously.[10] These bathochromic shifts seem to be attributable to the phenyl and thienyl groups. The cyclic voltammograms of **2a**,**b** (about 1.0×10^{-3} mol dm^{-3}) in dichloromethane containing 0.1 M (1 M = 1 mol dm^{-3}) tetrabutylammonium perchlorate at room temperature exhibited two quasi-reversible waves. The cyclic voltammogram of **2a** is shown in Figure 2. The first and second oxidation potentials vs. Ag/AgCl were +0.64 and +1.00 V for **2a** and +0.61 and +0.97 V for **2b**, respectively.

In contrast to the cases of **1a**,**b**, 2-*tert*-butylthio-3-pyrrolidinocyclopropenethione[4] and 2-phenyl-3-pyrrolidinocyclopropenethione[4] did not react with triphenylphosphine, but were recovered unchanged, this indicating that the addition of triphenylphosphine to these cyclopropenethiones does not occur owing to the presence of the pyrrolidinyl group.

As described above, it has been found that cyclopropenethiones bearing the *tert*-butylthio and aryl groups afford the thieno[3,4-*c*]thiophene system by reaction with triphenylphosphine.

References and Notes

1 N. Beye and M. P. Cava, *J. Org. Chem.*, **59**, 2223 (1994).

2 S. Yoneda, K. Ozaki, T. Inoue, A. Sugimoto, K. Yanagi, and M. Minobe, *J. Am. Chem. Soc.*, **107**, 5801 (1985).

3 T. Sugimoto, T. Nagatomi, H. Ando, and Z. Yoshida, *Angew. Chem. Int. Ed. Engl.*, **27**, 560 (1988); The yield of 2,3,5,6-tetraphenylthieno[3,2-*c*]thiophene: 9% (unpublished data).

4 Y. Yagyu, N. Matsumura, H. Tanaka, Z. Maeda, and H. Inoue, *J. Chem. Research (S)*, **1995**, 420.

5 Compound **1b** was prepared from bis(*tert*-butylthio)cyclopropenethione and 2-thienyl-lithium by the procedure similar to that in the preparation of **1a**.
Physical and spectroscopic data for **1b**: pale green crystals; mp 155-157 ℃ (from methanol); Found:C, 54.91;H, 4.91%. Calcd for $C_{11}H_{12}S_3$: C, 54.96; H, 5.03% ; IR (KBr) cm^{-1} 2950, 1750, 1324, 1306, 1255, 1168, 759 and 684; UV (λ max/nm in hexane, log ε) 350 (3.73), 274 (3.81), 242, (3.77) and 261 (3.74); ^{1}H NMR ($CDCl_3$) δ = 1.75 (s, 9H, *tert*-Bu), 7.27 (m, 1H) and 7.81 (m, 2H) ; ^{13}C NMR ($CDCl_3$) δ = 32.31, 51.54, 123.70, 129.04, 134.46, 134.96, 145.25, 152.83 and 168.89.

6 Physical and spectroscopic data for **2a**: red crystals; mp 177-178.5 ℃ (from methanol); Found: C, 66.55; H, 6.04%. Calcd for $C_{26}H_{28}S_4$: C, 66.62; H, 6.02% ; IR (KBr) cm^{-1} 2924, 1671, 1455, 1362 and 1163 ; UV (λ max/nm in hexane, log ε) 516 (4.34), 295 (4.36), 280 (4.31) and 248 (4.34) ; ^{1}H NMR ($CDCl_3$) δ = 0.94 (s, 18H, *tert*-Bu), 7.42 (m, 6H) and 7.70 (m, 4H) ; ^{13}C NMR ($CDCl_3$) δ = 30.17, 49.34, 110.30, 127.51, 127.61, 130.76, 131.45, 132.5 and 147.78.

7 Physical and spectroscopic data for **2b**: purple crystals; mp 199-201 ℃ (from methanol); Found: C, 54.80; H, 5.16%. Calcd for $C_{22}H_{24}S_6$: C, 54.96; H, 5.03%; IR (KBr) cm^{-1} 2955, 1458, 1362, 1163, 822 and 691; UV (λ max/nm in hexane, log ε) 538 (4.30), 297 (4.40) and 245 (4.38); ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H, *tert*-Bu), 7.13 (m, 2H), 7.35 (m, 2H) and 7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 30.12, 49.54, 111.12, 123.52, 126.35, 127.25, 129.90, 133.27 and 147.57.

8 Crystal data for **2a**: $C_{26}H_{28}S_4$, Fw = 468.77, triclinic, space group $P\bar{1}$, a = 11.640 (2), b = 9.733 (2), c = 5.6821(6) Å, α = 96.81 (1), β = 101.99 (1), γ = 105.86 (1)°, V = 595.1 (2) $Å^3$, Z = 1, Dx = 1.308 gcm^{-3}, μ (CuK α) = 3.683 mm^{-1}. A red crystal with dimensions of $0.075\times0.1\times0.2$ mm was used for data collection on a Rigaku AFC4 diffractometer with graphite monochromatized CuK α radiation (λ = 1.54184 Å). 2021 unique reflections were obtained up to 2 θ of 130°, and 1685 observed reflections ($|Fo|>3\sigma(F)$) were used for refinement. The structure was solved by a direct method using MULTAN78[11] and successive Fourier synthesis and refined by the block-diagonal least-square method using UNICSIII[12] to give R = 0.040 and wR = 0.039.

9 C. K. Johnson, ORTEP II . Report ORNL-5138. Oak Ridge Natl. Lab., Tennessee, U.S.A. (1976).

10 S. Yoneda, A. Tsubouchi, and K. Ozaki, *Nippon Kagaku Kaishi*, **7**, 1328 (1987).

11 P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M.M. Woolfson, MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Univs. of York, Endland and Louvain-la-Nerve, Belgium (1978).

12 T. Sakurai and K. Kobayashi , *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).