Reduction of 1,3,4,6-Tetrakis(alkylthio)thieno-[3,4-*c*]thiophenes with Sodium or Sodium Anthracenide Leading to the Cleavage of the Alkyl-Sulfur Bond

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The reaction of 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]thiophenes **1** with sodium or sodium anthracenide in hexamethylphosphoric triamide (HMPA) gave thieno[3,4-*c*]thiophene-1(3*H*)-thiones **2** by the cleavage of the alkyl-sulfur bond through the intermediary formation of their radical anions.

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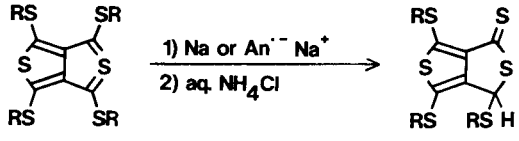
Thieno[3,4-*c*]thiophenes are an interesting class of compounds because of a nonclassical structure [1-9]. 1,3,4,6-Tetraphenyl- [4], 1,3,4,6-tetrathienyl- [6], and 1,3,4,6-tetrakis(alkylthio)- [7] thieno[3,4-*c*]thiophenes have been synthesized in a stable form and several reactions of these compounds have been reported [4,8,9,10]. However, the reaction with alkaline metals and aromatic radical anions has not been investigated as yet, except for the ESR research on the reduction of 1,3,4,6-tetraphenylthieno[3,4-*c*]-thiophene with potassium [10]. We carried out the reaction of 1,3,4,6-tetrakis(isopropylthio)- and 1,3,4,6-tetrakis-(*t*-butylthio)thieno[3,4-*c*]thiophenes (**1a,b**) with sodium and sodium anthracenide ($An^{\cdot-}$ Na^+) in hexamethylphosphoric triamide (HMPA). We now report our findings that the alkyl-sulfur bond of **1a,b** is cleaved through the intermediary formation of their radical anions by one-electron reduction.

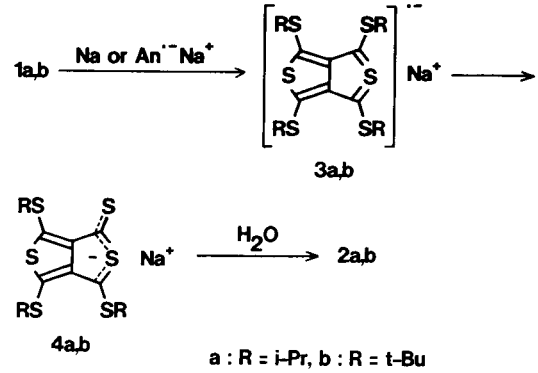


1a,b **2a,b**

a : R = i-Pr, b : R = t-Bu

A suspension of sodium (2 equivalents) in HMPA was stirred under argon at room temperature until a blue color appeared. After the compounds **1a,b** were added, the mixture was stirred at room temperature until the homogeneous solution was obtained. The solution was poured into saturated aqueous ammonium chloride solution and extracted with benzene. The products were separated by column chromatography on silica gel. The reaction with **1a** gave 3,4,6-tris(isopropylthio)thieno[3,4-*c*]thiophene-1(3*H*)-thione (**2a**) in 80% yield after 2 hours. In the case of **1b**, the thione **2b** was produced in 71% yield after 4 hours. The reaction time became longer than that in the case of **1a** because of low solubility. Furthermore, we carried out the reaction of **1a,b** with $An^{\cdot-}$ Na^+ which was prepared from anthracene and sodium in HMPA: the compounds **1a,b** were added under argon to a solution of ($An^{\cdot-}$ Na^+) in HMPA and the mixture was stirred for 2 hours at room temperature. The compounds **2a,b** were produced in 60 and 58% yields respectively. The ^1H nmr spectra of **2a,b** showed a singlet at δ 5.78 and 5.67 for H-3 respectively. Their ^{13}C nmr spectra showed the peaks due to the thiocarbonyl carbons of **2a,b** at δ 212.47 and 213.58 respectively. In addition, it was confirmed that **2a** was converted into **1a** in 78% yield by our method described previously [8], that is, by deprotonation with sodium hydride in dimethylformamide, followed by alkylation with isopropyl iodide.

The cyclic voltammograms of **1a,b** were measured in acetonitrile and dichloromethane solution [11], respectively, using platinum working electrode. The compound **1a** exhibited an reversible redox peak at $E_{1/2} = -1.53$ V *vs.* SCE. The difference in potentials between the cathodic and anodic current peaks was 60 mV. On the other hand, the cyclic voltammogram of **1b** showed an irreversible reduction peak at $E_{pc} = -1.72$ V *vs.* SCE without the corresponding oxidation peak, thus indicating that the cleavage of the *t*-butyl-sulfur bond occurs. The second reduction peaks of **1a,b** were not observed in the range of -1.50 to -2.10 V *vs.* SCE. Previously, it has been reported that the first reduction potential ($E_{1/2}$) of anthracene is -2.07 V *vs.* SCE in acetonitrile solution [12]. These facts indicate that the formation of the radical anions **3a,b** brings about the cleavage of their alkyl-sulfur bonds. This phenomenon was



a : R = i-Pr, b : R = t-Bu

in contrast to the fact that the radical cation and dication of **1a** do not bring about the cleavage of the isopropyl-sulfur bond [9].

The reaction is explained to proceed through the formation of the radical anions **3a,b**, followed by the cleavage of the alkyl-sulfur bond to give **4a,b**, which are converted into **2a,b** by protonation.

EXPERIMENTAL

Melting points were determined on a Yanaco MP-S3 melting point apparatus and are uncorrected. The ir spectra were recorded on a Hitachi 215 spectrometer. The uv spectra were obtained in a Shimadzu UV-160 spectrophotometer. The nmr spectra were recorded on a JEOL JNM-GX270 spectrometer. Chemical shifts are reported in ppm from TMS as an internal standard and given in δ units. The mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 70 eV by a direct-inlet system. The elemental analyses were recorded on a Yanaco MT-3 CHN recorder. The cyclic voltammetry of **1a** and **1b** was performed in acetonitrile solution containing tetraethylammonium perchlorate (0.1 *M*) and dichloromethane solution containing tetrabutylammonium perchlorate (0.1 *M*), respectively, in one-compartment cell with platinum working and counter electrodes and a saturated calomel reference electrode. The scan rate was 50 mV/s. Measurement was made with a Yanaco AC DC Cyclic Polarography P-900. Column chromatography was performed on silica gel (Wakogel C-300). The compounds **1a,b** were prepared according to the method described previously [7].

Reaction of Thieno[3,4-*c*]thiophenes **1a,b** with Sodium in HMPA.

Small pieces of sodium (9 mg, 0.40 mmole) were added under argon to HMPA (2 ml) and the mixture was stirred for 5 minutes at room temperature until a blue color appeared. After the compounds **1a,b** (0.2 mmole) were added over 5 minutes, the mixture was stirred at room temperature for 2 and 4 hours respectively. As the reaction proceeded, **1a,b** dissolved in HMPA. The solution was poured into saturated aqueous ammonium chloride solution (10 ml) and extracted with benzene. The organic layer was washed with water and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the residue was chromatographed on silica gel with dichloromethane-hexane (1:2, v/v) as an eluent to give thieno[3,4-*c*]thiophene-1(3*H*)-thiones **2a,b** in 80 and 71% yields respectively.

3,4,6-Tris(isopropylthio)thieno[3,4-*c*]thiophene-1(3*H*)-thione (**2a**).

This compound was obtained as an orange solid (hexane), mp 70-71°; ir (potassium bromide): 2970, 2920, 2865, 1430, 1380, 1215, 1160, 1085, 1055, 975 cm^{-1}; uv (hexane): λ max 281 nm (log ϵ 4.13), 300 sh (4.04), 359 (3.88), 400 (3.92); ^1H nmr (deuteriochloroform): δ 1.24, 1.35, 1.36, 1.37, 1.50, 1.51 (d, 3H, J = 6.7 Hz, SCHMe*Me*), 3.19, 3.35, 3.48 (sep, 1H, J = 6.7 Hz, SC*H*Me_2), 5.78 (s, 1H, 3-H); ^{13}C nmr (deuteriochloroform): δ 22.68, 23.00, 23.06, 23.78, 23.82, 36.62, 40.32, 42.38, 53.09, 124.13, 144.47, 147.48, 152.90, 212.47 (C=S); ms: 394 (M^+).

Anal. Calcd. for $C_{15}H_{22}S_6$: C, 45.65; H, 5.62. Found: C, 45.32; H, 5.41.

3,4,6-Tris(*t*-butylthio)thieno[3,4-*c*]thiophene-1(3*H*)-thione (**2b**).

This compound was obtained as a reddish purple solid (methanol-ethanol), mp 129.5-130.0°; ir (potassium bromide): 2950, 2925, 2860, 1515, 1455, 1415, 1365, 1205, 1160, 1055, 960, 775, 720 cm^{-1}; uv (hexane): λ max 286 nm (log ϵ 4.27), 300 sh (4.16), 366 (3.94), 400 sh (3.81); ^1H nmr (deuteriochloroform): δ 1.42, 1.45, 1.57 (s, 9H, SC*Me*$_3$), 5.67 (s, 1H, 3-H); ^{13}C nmr (deuteriochloroform): δ 30.63, 31.11, 31.28, 45.34, 49.21, 50.01, 51.27, 125.58, 143.61, 146.29, 153.70, 213.58 (C=S); ms: 436 (M^+).

Anal. Calcd. for $C_{18}H_{28}S_6$: C, 49.50; H, 6.46. Found: C, 49.26; H, 6.76.

Reaction of Thieno[3,4-*c*]thiophenes **1a,b** with Sodium Anthracenide in HMPA.

Small pieces of sodium (9 mg, 0.40 mmole) were added under argon to a suspension of anthracene (89 mg, 0.50 mmole) in HMPA (2 ml). After stirring for 2 hours at room temperature, the homogeneous blue solution of sodium anthracenid was obtained. The compounds **1a,b** (0.20 mmole) were added to the solution in one portion and the mixture was stirred for 2 hours at room temperature. The resulting solution was poured into saturated aqueous ammonium chloride solution (10 ml) and extracted with benzene. The extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of the solvent and chromatography of the residue with dichloromethane-hexane (1:2, v/v) as an eluent gave **2a,b** in 60 and 58% yields, respectively, along with many other products which were not identified.

Conversion of **2a** into **1a**.

A solution of **2a** (50 mg, 0.13 mmole) in dimethylformamide (1 ml) was added under nitrogen to a suspension of sodium hydride (6.1 mg, 0.26 mmole) in dimethylformamide (5 ml) at room temperature. The mixture was stirred for 0.5 hours and then isopropyl iodide (43 mg, 0.16 mmole) was added with stirring. After 0.5 hours, the mixture was poured into water and extracted with dichloromethane. The extract was washed with water, dried over anhydrous sodium sulfate, and the solvent was evaporated under reduced pressure to give **1a** in 78% yield as a red solid. Recrystallization from methanol gave pure red needle.

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REFERENCES AND NOTES

[1] Cava and M. L. Lakshmikanthan, *Acc. Chem. Res.*, **8**, 138 (1975).

[2] C. A. Ramsden, Comprehensive Heterocyclic Chemistry, Vol **6**, K. T. Potts, ed, Pergamon Press, 1984, p 1027.

[3] M. P. Cava, N. M. Pollack and G. A. Dieterle, *J. Am. Chem. Soc.*, **95**, 2558 (1973).

[4] M. P. Cava, M. Beforouz, G. E. M. Husbands and M. Srinivasan, *J. Am. Chem. Soc.*, **95**, 2561 (1973).

[5] J. Nakayama, A. Ishii, Y. Kobayashi and M. Hoshino, *J. Chem. Soc., Chem. Commun.*, 959 (1988).

[6] A. Ishii, J. Nakayama, J. Kazama, Y. Ida, T. Nakamura and M. Hoshino, *J. Org. Chem.*, **56**, 78 (1991).

[7] S. Yoneda, K. Ozaki, A. Tsubouchi and H. Kojima, *J. Heterocyclic Chem.*, **25**, 559 (1988).

[8] A. Tsubouchi, N. Matsumura and H. Inoue, *J. Chem. Soc., Perkin Trans. 1*, 909 (1991).

[9] A. Tsubouchi, C. Kitamura, N. Matsumura and H. Inoue, *J. Heterocyclic Chem.*, **28**, 1643 (1991).

[10] R. Gleiter, R. Bartetzko, G. Brähler and H. Bock, *J. Org. Chem.*, **43**, 3893 (1978).

[11] The compound **1a** is insoluble in acetonitrile.

[12] N. L. Holy, *Chem. Rev.*, **74**, 243 (1974).