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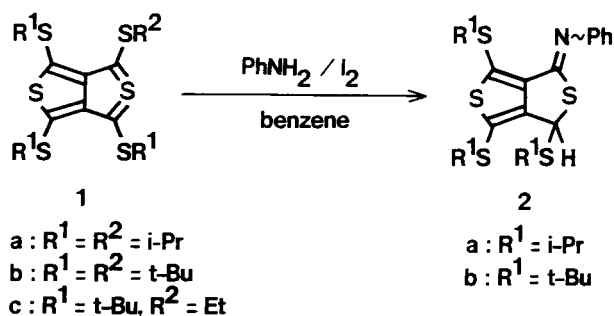
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1,3,4,6-Tetrakis(alkylthio)thieno[3,4-*c*]thiophenes were oxidized by iodine in the presence of aniline in dry benzene to give 1,4,6-tris(alkylthio)thieno[3,4-*c*]thiophen-3(1*H*)-imines in high yields through the intermediary formation of their cation radicals.

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Thieno[3,4-*c*]thiophenes are of interest in having a non-classical structure with 10  $\pi$ -electrons [1-8]. Recently we have synthesized 1,3,4,6-tetrakis(alkylthio)thieno[3,4-*c*]thiophenes in a stable form by dimerization of 2,3-bis(alkylthio)cyclopropenethiones [7]. Furthermore, we have disclosed that the first and the second oxidation potentials of 1,3,4,6-tetrakis(isopropylthio)thieno[3,4-*c*]thiophene (**1a**) are  $E_{1/2}^1 = +0.19$  V and  $E_{1/2}^2 = +0.54$  V vs. SCE, respectively, by the measurement of the cyclic voltammogram of **1a** in acetonitrile (MeCN) solution [9]. On the basis of this fact, we investigated the oxidation of thieno[3,4-*c*]thiophenes with iodine ( $E_{1/2}^{\text{red}} = +0.40$  V vs. SCE [10]) in the presence of aniline which can react with an oxidation intermediate. We now report our findings that the reactions with **1a** and 1,3,4,6-tetrakis(*t*-butylthio)- or 1,4,6-tris(*t*-butylthio)-3-(ethylthio)thieno[3,4-*c*]thiophene (**1b,c**) in dry benzene give 1,4,6-tris(isopropylthio)- and 1,4,6-tris(*t*-butylthio)thieno[3,4-*c*]thiophen-3(1*H*)-imines (**2a,b**), respectively, in high yields through the intermediary formation of their cation radicals.

Scheme 1

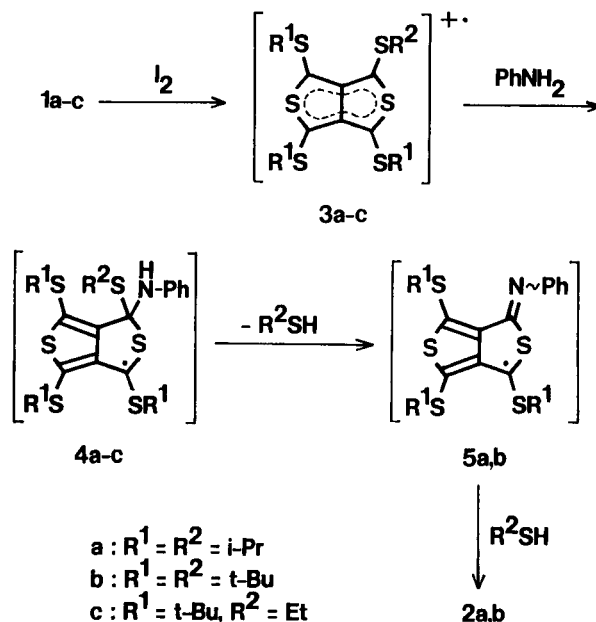


The reactions were carried out as follows: a solution of iodine in dry benzene was slowly added to a solution of a mixture of **1a-c** and aniline in dry benzene and the mixture was stirred at room temperature. The solvent was removed and the products were separated by column chromatography on silica gel with dichloromethane-hexane (1:1) as an eluent. The reaction with **1a** gave the thieno[3,4-*c*]thiophen-3(1*H*)-imine **2a** in a quantitative yield after 1 hour. The compounds **1b,c** were converted into **2b** in 62

and 84% yields after 41 and 5 hours, respectively. In the case of **1b**, the starting material was recovered in 14% yield. The  $^1\text{H}$  nmr spectra of **2a,b** showed a singlet at  $\delta$  5.67 and 5.58, respectively, for a proton attached to the carbon in the 1-position. The ir spectra of **2a,b** showed the absorption due to the C=N bond at 1620 and 1630  $\text{cm}^{-1}$  respectively. Although benzylamine and butylamine were used instead of aniline, the reaction did not occur at all, but **1a** was recovered unreacted, because of the formation of the complexes between these amines and iodine. Furthermore, the esr spectrum of a solution of a mixture of **1a** and iodine in acetonitrile showed five lines due to the coupling of four equivalent methine protons of the isopropylthio groups;  $g = 2.0045$  and  $a_H = 0.056$  mT. This result indicates that **1a** is oxidized to its cation radical by iodine.

The reaction is explained to proceed through the formation of the cation radical **3a-c** by one-electron oxidation of **1a-c** with iodine, as shown in Scheme 2. The cation radicals **3a-c** react with aniline to give the radicals **4a-c**, which

Scheme 2



are converted into **5a,b** by the elimination of thiols. The abstraction of hydrogen from thiols by **5a,b** leads to the formation of **2a,b**. The cation radical of **1c** was found to react with aniline at the position having the ethylthio group.

### 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 on 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 the  $\delta$  units. The mass spectra were recorded on a Shimadzu LKB-9000 spectrometer operating at 70 eV by a direct-inlet system. The esr spectrum was obtained on a JEOL JES-RE2X spectrometer. Elemental analyses were recorded on a Yanaco MT-3 CHN recorder. Column chromatography was performed on silica gel (Wakogel C-300). The compounds **1a-c** were prepared according to the method described previously [7,8].

#### General Procedure for the Oxidation of Thieno[3,4-*c*]thiophenes **1a-c** with Iodine in the Presence of Aniline.

A solution of iodine (15 mg, 0.060 mmole) in dry benzene (5 ml) was added under nitrogen to a solution of a mixture of **1a-c** (0.010 mmole) and aniline (21 mg, 0.23 mmole) in dry benzene (10 ml) at room temperature. The mixture was stirred at room temperature and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel with dichloromethane-hexane (1:1, v/v) as an eluent to give **2a,b**.

#### *N*-Phenyl-1,4,6-tris(isopropylthio)thieno[3,4-*c*]thiophen-3(1*H*)-imine (**2a**).

This compound was obtained from **1a**, iodine and aniline in 100% yield after 1 hour as a colorless oil; ir (neat): 3050, 2960, 2910, 2855, 1620 (C=N), 1580, 1520, 1485, 1440, 1380, 1365, 1240, 1220, 1150, 1050, 1015, 990, 905, 840, 765, 725  $\text{cm}^{-1}$ ; uv (dichloromethane):  $\lambda$  max 253 nm ( $\log \epsilon$  4.40), 335 (3.91);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.21, 1.33, 1.34, 1.35, 1.45 and 1.51 (d, 3H,  $J = 6.7$  Hz, SCHMeMe), 3.15, 3.35 and 3.62 (sep, 1H,  $J = 6.7$  Hz, SCHMe<sub>2</sub>), 5.67 (s, 1H, 1-H), 7.06-7.38 (m, 5H, Ph);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  22.67, 23.08, 23.22, 23.56, 23.64, 23.72, 36.56, 40.06, 42.20, 49.46, 120.49, 124.74, 125.38, 129.02, 137.84, 138.95, 150.89, 151.42, 157.77; ms: 453 ( $M^+$ ).

*Anal.* Calcd. for C<sub>21</sub>H<sub>27</sub>NS<sub>3</sub>: C, 55.59; H, 6.00; N, 3.09. Found: C, 55.81; H, 6.30; N, 3.14.

#### *N*-Phenyl-1,4,6-tris(*t*-butylthio)thieno[3,4-*c*]thiophen-3(1*H*)-imine (**2b**).

This compound was obtained from **1b**, iodine and aniline in 62% yield after 41 hours as a pale yellow solid, mp 149-150°, accompanied by recovery of **1b** in 14% yield, ir (potassium bromide): 3020-2869, 1630 (C=N), 1595, 1475, 1365, 1180, 775, 695  $\text{cm}^{-1}$ ; uv (dichloromethane):  $\lambda$  max 250 nm ( $\log \epsilon$  4.48);  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.41 (s, 18H, 2 x SC(CH<sub>3</sub>)<sub>3</sub>), 1.47 (s, 9H, SC(CH<sub>3</sub>)<sub>3</sub>), 5.58 (s, 1H, 1-H), 7.00-7.37 (m, 5H, Ph);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  30.96, 31.11, 31.21, 45.25, 47.82, 48.95, 50.24, 120.13, 124.55, 129.00, 129.41, 133.29, 143.50, 151.80, 152.25, 157.97; ms: 495 ( $M^+$ ).

*Anal.* Calcd. for C<sub>22</sub>H<sub>33</sub>NS<sub>3</sub>: C, 58.17; H, 6.71; N, 2.82. Found: C, 57.96; H, 6.81; N, 2.62.

This compound was also obtained from **1c**, iodine and aniline in 84% yield after 5 hours.

#### Measurement of the ESR Spectrum.

Iodine (0.6 mg, 0.002 mmole) was added under argon to a suspended solution of **1a** (1 mg, 0.002 mmole) in degassed acetonitrile (1 ml) at -30°. After the mixture became homogeneous, the esr spectrum was measured at room temperature. The *g*-value and hyperfine splitting constant were determined by comparison with those of 1,1-diphenyl-2-picrylhydrazyl and potassium nitrosodisulfonate.

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