*Chemistry of Heterocyclic Compounds, Vol. 33, No. 9, 1997*

# TAUTOMERISM AND SELF-CONVERSION OF SUBSTITUTED 2-THIOPHENETHIOLS. SUBSTITUENT EFFECTS AND SELF-THIYLATION MECHANISM

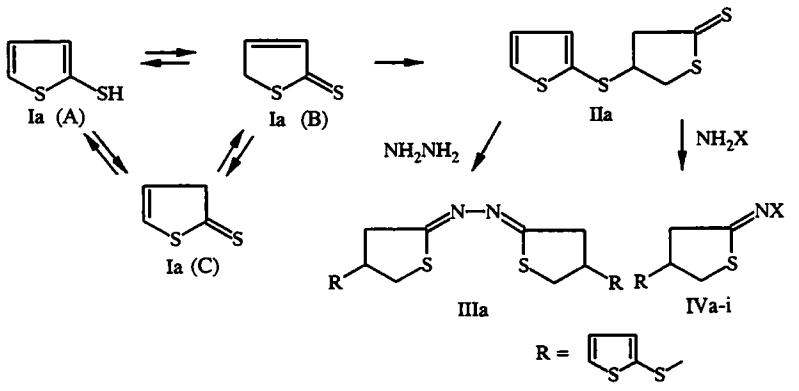
**V. Yu. Vvedenskii, E. D. Shtefan, R. N. Malyushenko, E. V. Shilkin, and É. N. Deryagina**

*The substituent effect on the self-thiylation of 2-thiophenethiols was studied. Experimental results and quantum chemical calculations suggested possible mechanisms for this reaction dependent on the reaction conditions.*

We have already discovered the self-thiylation of 2-thiophenethiol (Ia) to give a dimeric dithiolactone (IIa) [1-4]. Subsequently, we obtained products of the reaction of IIa with hydrazine (IIIa) and its derivatives (IVa-h) as well as with hydroxylamine (IVi) (see our previous work [5] and present communication).

Similar to dithiolactone IIa, γ-dithiobutyrolactone reacts with hydrazine hydrate and acetone monohydrazone to give III (V, R = H) and IV (VI, R = H, X = N=$CMe_2$), respectively (see Scheme 1).

Scheme 1




IV a X = NHPh; b X = NHEt; c X = NHPr-*i*; d X = $NHC_6H_3(NO_2)_2$-2,4; e X = NHC(=S)$NH_2$; f X = NHC(=O)Ph; g X = N=$CMe_2$; n X = N=$C_5H_8$-cyclo, i X = OH

In the present work, we elucidated the substituent effect on the self-thiylation of substituted thiophenethiols (Ib-p) under different conditions (see Table 1). The methods of synthesis and indices for thiols Ib-p are given in Table 2, while the indices for their products are given in Tables 3 and 4. PMR spectroscopy was used to detect products II and IV. Characteristic signals for dithiobutyrolactone ring protons were found in the aliphatic region of the spectra of these compounds (see Table 3 and the figure for the spectrum of IIa given in our previous work [1]).

The use of gas–liquid chromatography and GC/MS is difficult since the "dimers" convert to the starting monomers as seen in the case of IIa [1]. Except for 4-methyl-2-thiophenethiol Ig, which converts to "dimer" IIb even under ordinary conditions, the other thiols studied do not give self-thiylation products upon heating or the action of catalysts. However, the

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of Russia, 664033 Irkutsk, Russia.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1203-1218, September, 1997. Original article submitted September 13, 1996; revision submitted April 3, 1997.

0009-3122/97/3309-1047$18.00 

TABLE 1. Substituent Effect on the Self-Thiylation of R-Substituted 2-Thiophenethiols Ia-p

| Thio | | Reaction conditions and | | | | |
|---|---|---|---|---|---|---|
| Number | R | 20 °C | 50 °C | catalysis by $Et_3N$ | $H_2NNHPh$ 20 °C, 48 h | $H_2NNPh$ 60 °C, 1 h |
| Ia | H | IIa (70...90) | IIa (70...90) | IIa (> 95) | IVa (99) [5] | |
| Ib | 3-All | — | — | — | — | |
| Ic | 3-Br | *[2] | *[2] | *[2] | | |
| Id | 5-Cl | *[2] | *[2] | *[3] | *[3] | |
| Ie | 5-Et | — | — | — | — | IVj (43)*[4] |
| If | 3-Me | — | — | — | | IVk (> 95) |
| Ig | 4-Me | IIb (65...80) | IIb 65...80) | IIb (> 90) | IV*l* (> 95) | |
| Ih | 5-Me | — | — | — | — | IVm (> 95) |
| Ii | 5-MeS | — | — | — | — | IVn (> 95) |
| Ij | 5-SH | — | — | — | — | — |
| Ik | 3-Ph | — | — | — | — | — |
| *Il* | 4-Ph | — | — | — | — | — |
| Im | 5-Ph | — | — | — | — | — |
| In | 5-Het*[5] | — | — | — | — | — |
| Io | 5-$Me_3Si$ | — | — | — | Ia (96) | Ie (67)*[4] |
| Ip | 5-Bu-*t* | — | — | — | — | — |

*Product (yield, %), no self-thiylation.

*[2]Starting thiol decomposes with release of HHal [6, 7].

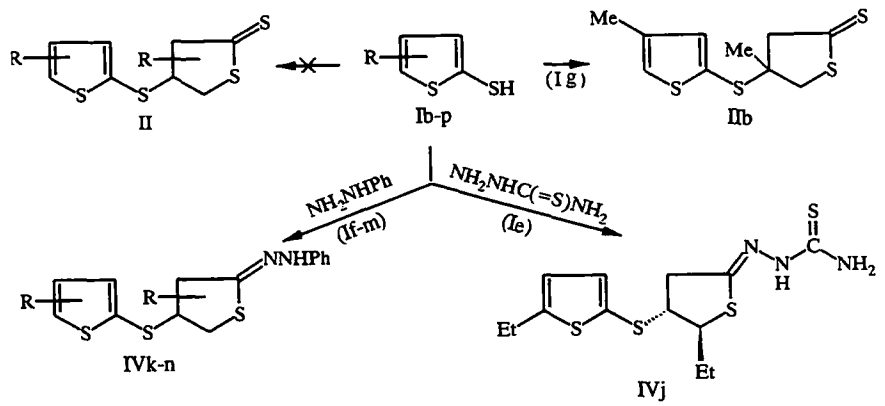
*[3]Mixture of disulfides formed [8].

*[4]Thiosemicarbazide used instead of phenylhydrazine. The product yield after recrystallization from methanol is given.

*[5]Het = 2′-thienyl.

reaction of 3-Me-, 4-Me-, 5-Me-, and 5-MeS-substituted thiophenethiols If-i with a stoichiometric amount of phenylhydrazine gave derivatives of dimeric products IVj-m as ~15:85 mixtures of the *cis* and *trans* isomers. Similarly, IVj was synthesized from thiol Ie and thiosemicarbazide (see Scheme 2).

Scheme 2




IVk R = Me (3 and 3′); *l* R = Me (4 and 4′); m R = Me (5 and 5′); n R = MeS (5 and 5′)

TABLE 2. Synthesis Method and Indices of R-Substituted 2-Thiophenethiols Ie-p*

| Compound | Synthesis method *2 | mp, °C (mm, Hg) | Mass spectrum,' $M^+$, m/z (%) | PMR spectrum, δ, ppm, coupling constant (J), Hz | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | | | 2-SH | 3-H(R) | 4-H (R) | 5-H (R) | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Ic | PhLi/S/H$^+$ | 83 (13), Ref. [13] 84 (13) | 144 (100) | 4,32 s | 7,03 d, $J_{34}$ = 3,5 | 6,81 d. t, $J_{4CH2}$ = 1,1 | 1,37 t, $J$ = 7,5 (Me), 2,9 d. q ($CH_2$) | 43 |
| If | TMS/$H_2O$ | 86 (30), Ref. [10] 86 (30) | 130 (100) | 3,17 s | 2,27 s (Me) | 6,85 d, $J_{45}$ = 5,3 | 7,17 d | 100 |
| Ig*3 | PhLi/S/H$^+$ | 65...67 (12), Ref. [10] 76...78 (14) | 130 (100) | 3,48 s | 6,84 d, $J_{35}$ = 1,3 | 2,19 s (Me) | 6,89 m | 29 |
| Ih*4 | BuLi/S/H+ | 77 (20) Ref. [14] 64 (10) | 130 (100) | 3,45 m | 6,90 d. d, | 6,59 m | 2,43 d. d (Me) | 23 |
| Ii | TMS/$H_2O$ | 102 (1)*5 Ref. [10] 84 (0,4) | 162 (100) | 4,50 s | 6,95 s | 6,95 s | 2,46 s (MeS) | 100 |
| Ij | TMS/$H_2O$ | 85 (5) Ref. [15] 85 (5) | 148 (100) | 3,64 s | 7,00 s | 7,00 s | 3,64 s (SH) | 100 |
| Ik*6 | BuLi/S/H+ | 95...105(1) | 192 (100) | 3,48 d. d, $J_{SH4}$ = 0,35, $J_{SH5}$ = 0,65 | 7,31 m (1H, $p$-H Ph), 7,41 m (2H, $m$-H Ph), 7,53...7,56 m (2H, $o$-H Ph) | 7,12 d. d, $J_{45}$ = 5,5 | 7,28 d. d | 17 |
| Il*6 | BuLi/S/H+ | 95...105 (1) | 192 (100) | 3,61 d. d, $J_{SH3}$ = 1,6, $J_{SH5}$ = 0,9 | 7,40 t, $J_{35}$ = 1,6 | 7,37 m (1H, $p$-H Ph), 7,46 m (2H, $m$-H Ph), 7,53...7,56 m (2H, $o$-H Ph) | 7,38 d. d | 24 |

TABLE 2 (continued)

| Compound | Synthesis method *2 | mp, °C (mm, Hg) | Mass spectrum, $M^+$, m/z (%) | PMR spectrum, δ, ppm, coupling constant (J), Hz | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|
| | | | | 2-SH | 3-H(R) | 4-H (R) | 5-H (R) | |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Im | BuLi/S/$H^+$ | 95...105 (1) | 192 (100) | 4,59 s | 7,18 d, $J_{34}$ = 3,8 | 7,10 d | 7,3...7,7 m (Ph) | 38 |
| In*7 | PhLi/S/$H^+$*8 Cp. [16] | 118 (1) | 198 (100) | 3,55 d, $J_{4SH}$ = 1,4 | 6,80 d.d, $J_{34}$ = 3,7 | 6,98 d | 7,12 d. d (3'-Hhet), 7,00 d.d (4'-Hhet), 7,21 d.d (5'-Hhet), $J_{3',4'}$ = 3,6, $J_{3',5'}$ = 1,2, $J_{4',5'}$ = 5,1 | 41 |
| Io*9 | TMS/$H_2O$ | 75 (2) | 188 (40,2) | 3,51 d, $J_{3SH}$ = 1,0 | 7,07 d, $J_{34}$ = 3,4 | 7,03 d | 0,269 s ($Me_3Si$) | 100 |
| Ip *10 | BuLi/$H^+$ | 71 (2) | | 3,93 d, $J_{3SH}$ = 1,2 | 6,88 d, $J_{34}$ = 3,7 | 6,69 d | 1,34 s (*t*-Bu) | 73 |

*Indices of thiols Ia [1], Ib [9], Ic [10], and Id [6] given previously.

*2BuLi/S/$H^+$, PhLi/S/$H^+$) product obtained by consecutive treatment of the corresponding substituted thiophene with *n*-butyl- or phenyllithium, sulfur, and HCl according to Jones [6]; TMS/$H_2O$) product obtained by hydrolysis of the corresponding silyl ether (see Table 5 and our previous work [11, 12]).

*3Contains 20% impurity of thiol If; total yield of Ig + If given.

*4 $^{13}C$ NMR spectrum: 143.84 (C—SH), 134.54 (C=C—SH), 125.75 (C=C—$CH_3$), 121.26 (C—$CH_3$), 15.52 ($CH_3$).

*5$n_D^{20}$ = 1.6630.

*6Product obtained as a 7:10 mixture of Ik + Il, 41% total yield.

*7 $^{13}C$ NMR spectrum: 123.7, 124.02, 124.07, 124.8, 127.9, 134.81, 136.87, 140.74. Found: C, 48.26; H, 3.17; S, 48.72%. Calculated for $C_8H_6S_3$: C, 48.45; H, 3.05; S, 48.50%.

*8A two-fold excess of 2,2'-dithienyl was used to prevent the formation of 5,5'-dithiol.

*9Found: C, 44.42; H, 6.37; S, 34.02, Si, 15.17%. Calculated for $C_7H_{12}S_2Si$: C, 44.63; H, 6.42; S, 34.04; Si, 14.91%.

*10Found: C, 56.93; H, 6.94; S, 37.02%. Calculated for $C_8H_{12}S_2$: C, 56.77; H, 7.02; S, 37.21%.

TABLE 3. Indices of Tetrahydrothiophenes IVb-n, V, and VI

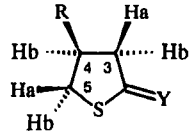
| Compound | Name | Found, % | | | | Chemical formula | Calculated, % | | | | $M^+$ | mp, °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | S | | C | H | N | S | | |
| IIb | 4-(4-Methyl-2-thienylthio)-4-methyltetrahydrothiophene-2-thione | 45,97 | 4,53 | — | 49,34 | $C_{10}H_{12}S_4$ | 46,12 | 4,64 | | 49,24 | 260 | * |
| IIIa | Azinodi[4-(2-thienylthio)-2-tetrahydrothiophene] | 44,67 | 3,70 | 6,48 | 44,91 | $C_{16}H_{16}N_2S_6$ | 44,83 | 3,76 | 6,53 | 44,87 | — | 179...180 |
| IVb | 4-(2-Thienylthio)-2-ethylhydrazonotetrahydrothiophene | 46,32 | 5,38 | 10,81 | 37,45 | $C_{10}H_{14}N_2S_3$ | 46,48 | 5,46 | 10,84 | 37,22 | 258 | * |
| IVc | 4-(2-Thienylthio)-2-isopropylhydrazonotetrahydrothiophene | 48,29 | 5,75 | 10,15 | 35,43 | $C_{11}H_{16}N_2S_3$ | 48,50 | 5,92 | 10,28 | 35,30 | 272 | * |
| IVd | 4-(2-Thienylthio)-2-(2,4-dinitrophenyl)hydrazonotetrahydrothiophene | 42,23 | 2,95 | 13,98 | 24,37 | $C_{14}H_{12}N_4O_4S_3$ | 42,41 | 3,05 | 14,13 | 24,26 | — | 138...140 |
| IVe | 4-(2-Thienylthio)-2-thiosemicarbazonotetrahydrothiophene | 37,15 | 3,75 | 14,43 | 44,38 | $C_9H_{11}N_3S_4$ | 37,35 | 3,83 | 14,52 | 44,31 | — | 140...142 |
| IVf | 4-(2-Thienylthio)-2-benzoylhydrazonotetrahydrothiophene | 53,65 | 4,10 | 8,23 | 28,85 | $C_{15}H_{14}N_2OS_3$ | 53,87 | 4,22 | 8,38 | 28,76 | — | 76...78 |
| IVg | 2-(N'-Isopropylidenehydrazino)-4-(2-thienylthio)tetrahydrothiophene | 48,75 | 5,02 | 10,23 | 35,64 | $C_{11}H_{14}N_2S_3$ | 48,86 | 5,22 | 10,36 | 35,57 | 270 | * |
| IVh | 2-(N'-Cyclopropylidenehydrazino)-4-(2-thienylthio)tetrahydrothiophene | 52,54 | 5,33 | 9,35 | 32,53 | $C_{13}H_{16}N_2S_3$ | 52,67 | 5,44 | 9,45 | 32,44 | 296 | * |
| IVi | 2-Oximino-4-(2-thienylthio)-tetrahydrothiophene | 41,43 | 3,78 | 5,98 | 41,73 | $C_8H_9NOS_3$ | 41,53 | 3,92 | 6,05 | 41,57 | 231 | 119...120 |

TABLE 3 (continued)

| Compound | Name | Found, % | | | | Chemical formula | Calculated, % | | | | M+ | mp, °C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | H | N | S | | C | H | N | S | | |
| IVj | 4-(5-Ethyl-2-thienylthio)-2-thiosemicarbazono-5-ethyltetrahydrothiophene | 45,10 | 5,44 | 11,85 | 37,39 | $C_{13}H_{19}N_3S_4$ | 45,19 | 5,54 | 12,16 | 37,11 | — | 168...170 |
| IVk | 4-(3-Methyl-2-thienylthio)-2-phenylhydrazono-3-methyltetrahydrothiophene | 57,25 | 5,77 | 8,20 | 28,63 | $C_{16}H_{18}N_2S_3$ | 57,45 | 5,42 | 8,37 | 28,75 | | * |
| IVl | 4-(4-Methyl-2-thienylthio)-2-phenylhydrazono-4-methyltetrahydrothiophene | 57,20 | 5,30 | 8,15 | 28,45 | $C_{16}H_{18}N_2S_3$ | 57,45 | 5,42 | 8,37 | 28,75 | | * |
| IVm | 4-(5-Methyl-2-thienylthio)-2-phenylhydrazono-5-methyltetrahydrothiophene | 57,29 | 5,77 | 8,29 | 28,61 | $C_{16}H_{18}N_2S_3$ | 57,45 | 5,42 | 8,37 | 28,75 | | * |
| IVn | 4-(5-Methylthio-2-thienylthio)-2-phenylhydrazono-5-methylthiotetrahydrothiophene | 48,15 | 4,98 | 6,99 | 40,25 | $C_{16}H_{18}N_2S_5$ | 48,21 | 4,55 | 7,03 | 40,21 | | * |
| IVo | 4-(3-Methyl-2-thienylthio)-2-phenylhydrazono-4-methyltetrahydrothiophene | 57,03 | 5,81 | 8,31 | 28,79 | $C_{16}H_{18}N_2S_3$ | 57,45 | 5,42 | 8,37 | 28,75 | | * |
| V | Azinodi(2-tetrahydrothiophene) | 47,85 | 6,15 | 13,93 | 32,30 | $C_8H_{12}N_2S_2$ | 47,97 | 6,04 | 13,98 | 32,01 | 200 | 195...197 |
| VI | 2-(N'-Isopropylidenehydrazino)-tetrahydrothiophene | 53,79 | 7,73 | 17,84 | 20,63 | $C_7H_{12}N_2S$ | 53,81 | 7,74 | 17,93 | 20,52 | 156 | * |

*Viscous oil; (—) mass spectrum could not be obtained due to low volatility of the sample.

TABLE 4. PMR Spectra, $\delta$, ppm, Coupling Constant ($J$, Hz, see [17]) of Tetrahydrothiophene Derivatives* (see Schemes 1 and 2)




| Compound | R*2 | 3-H(R)a | 3-H(R)b | 4-H(R)b | 5-H(R)a | 5-H(R)b | $J_{3a3b}$ | $J_{3a4b}$ | $J_{3b4b}$ | $J_{5a5b}$ | $J_{4b5a}$ | $J_{4b5b}$ | Y |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| IIb | 6,8 d; 7,1 d. q ($2H_{Het}$); 2,26 d, $J$ = 1,2 (3H, Me) | 3,02 d | 3,21 d | 1,58 s (3H, Me) | 3,45 d | 3,84 d | -17,8 | 0,0 | 0,0 | -11,7 | 0,0 | 0,0 | |
| IIIa | 7,00 d.d; 7,17 d.d; 7,41 d.d ($6H_{Het}$) | 2,79 d.d | 3,11 m | 3,66 m | 3,11 m | 3,27 d.d | -16,0 | 9,6 | —*4 | -11,0 | — | 6,0 | |
| IVb *3 | 7,10 d.d; 7,27 d.d; 7,64 d.d ($3H_{Het}$) | 2,61 d.d | 3,10...3,30 m | 3,73 m | 3,10...3,30 m | 3,46 d.d | -15,5 | 8,5 | — | -11,0 | — | 5,5 | 1,08 t (3H, Me); 2,62 q ($CH_2$); 4,20 br.s (NH) |
| IVc | 7,10 d.d; 7,27 d.d; 7,64 d.d ($3H_{Het}$) | 2,60 d.d | 2,93 d.d | 3,73 m | 3,16 d. d | 3,45 d.d | -15,5 | 9,5 | 6,5 | -11,4 | 7,2 | 5,5 | 1,08 d (3H, Me); 3,30 m (CH); 4,15 br.s (NH) |
| IVd | 7,15 d,d; 7,34 d. d; 7,70 d.d ($3H_{Het}$) | 2,98 d.d | 3,33 d.d | 4,04 m | 3,50 d. d | 3,83 d.d | -16,2 | 7,0 | 6,2 | -11,5 | 6,3 | 5,3 | 7,85 ($o$-H Ph); 8,4 and 8,99 ($2m$-H Ph); 10,45 br.s (NH) |

TABLE 4 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IVe | 7,12 d.d; 7,31 d.d; 7,67 d.d ($3H_{Het}$) | 2,79 d.d | 3,11 d.d | 3,92 m | 3,38 d.d | 3,69 d.d | -16,0 | 7,5 | 6,1 | -11,5 | 6,8 | 5,3 | 7,42 br.s ($NH_2$); 8,35 br.s (NH) |
| IVf*[5] | 7,02 d.d; 7,20 d.d; 7,76 d.d ($3H_{Het}$) | 2,88 d.d | 3,20...3,35 m | 3,70 m | 3,20...3,35 m | 3,52 d.d | -16,0 | 9,5 | — | -10,5 | — | 6,5 | 7,4...7,5 m (5H Ph); 8,19 br.s (NH) |
| IVg | 7,10 d.d; 7,27 d.d; 7,63 d.d ($3H_{Het}$) | 2,73 d.d | 3,00...3,20 m | 3,80 m | 3,00...3,20 m | 3,35 d.d | -16,5 | 8,5 | — | -11,5 | — | 5,5 | 1,94 s (3H, Me); 1,96 s (3H, Me) |
| IVh | 7,12 d.d; 7,29 d.d; 7,66 d.d ($3H_{Het}$) | 2,73 d.d | 3,00...3,15 m | 3,83 m | 3,00...3,15 m | 3,37 d.d. | -16,5 | 8,5 | — | -11,5 | — | 5,5 | 1,74 m (4H, $CH_2CH_2CH_2$; 2,05 m (4H, $CH_2C$=) |
| IVi | 7,11 d.d; 7,29 d.d; 7,65 d.d ($3H_{Het}$) | 2,64 d.d | 2,97 d.d | 3,79 m | 3,09 d.d | 3,38 d.d | -15,4 | 7,8 | 5,9 | -11,4 | 7,2 | 5,4 | 10,02 s (NOH) |
| IVj | 6,84 d. t; 7,12 d ($2H_{Het}$); 1,28 t, $J$ = 7,4 (3H, Me); 2,85 d. q, $J$ = 1,1 (2H, $CH_2$); $J_{34}$ = 4,1 | 2,85 d.d | 3,14 d.d | 3,46 d.d.d | 3,71 d.d.d | 1,03 t (Me) $J$ = 7,4; 1,71 d.d.q; 2,21 d. d. q $CH_2$, $^{gem}J_{CH_2}$ = 14,7 | -16,0 | 8,9 | 6,2 | 9,3 | 7,7 | 0,0 | 7,40 br.s ($NH_2$), 7,94 br.s (NH) |
| IVk | 6,76 d; 7,26 d: ($2H_{Het}$); 2,25 s (3H, Me) | 2,61 m | 1,42 d (3H, Me) | 2,92 m | 3,09 t | 3,28 d.d | 6,5 | 8,5 | 0,0 | -11,0 | 10,9 | 6,0 | 6,34 br.s (NH); 6,80...7,24 m (5H Ph) |

TABLE 4 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IVl | 6,80...7,40 m ($2H_{Het}$); 2,25 d; $J$ = 0,5 (3H, Me) | 2,80 d | 3,01 d | 1,54 s (3H, Me) | 3,16 d | 3,47 d | -15,5 | 0,0 | 0,0 | -11,4 | 0,0 | 0,0 | 6,37 br.s (NH); 6,80...7,40 m (5H Ph) |
| IVm | 6,70...7,20 m ($2H_{Het}$); 2,47 d; $J$ = 1,2 (3H, Me) | 2,90...3,30 m | 2,90...3,30 m | 2,90...3,30 m | 3,69 d.q | 1,54 d (3H, Me) | — | — | — | 6,6 | 7,2 | 0,0 | 6,70...7,20 m (5H Ph); 7,42 br. s (NH) |
| IVn | 6,60...7,60 m ($2H_{Het}$); 2,45 s (MeS) | 2,96 d.d | 3,37 d.d | 3,58 m | 4,64 d | 2,15 s (3H, MeS) | -15,6 | 6,7 | 6,4 | 0,0 | 5,8 | 6,4 | 6,35 br. s (NH); 6,60...7,60 m (5H Ph) |
| IVo | 6,80...7,40 m ($2H_{Het}$); 2,34 d; $J$ = 1,0 (3H, Me) | 2,80 d | 2,98 d | 1,54 s (3H, Me) | 3,19 d | 3,50 d | -15,5 | 0,0 | 0,0 | -11,4 | 0,0 | 0,0 | 6,34 br.s (NH); 6,80...7,40 m (5H Ph) |
| V | 2,08 m (2H, 4-$H_a$) | 2,68 | 2,68 | 2,08 m | 3,06 | 3,06 | 0,0 | 7,0 | 7,0 | 0,0 | 6,5 | 6,5 | |
| VI | 2,08 m (1H, 4-$H_a$) | 2,67 t | 2,67 t | 2,08 m | 3,05 t | 3,05 t | 0,0 | 7,0 | 7,0 | 0,0 | 6,5 | 6,5 | 1,92 s (3H, Me); 1,94 s (3H, Me) |

*The proton signals of identical fragments attached by an =N—N= bridge in symmetrical compounds IIIa and V are equivalent.

*2R = H/R'-thien-2-yl (Het); the coupling constants of the Het protons have ordinary values: 5.3, 3.5, and 1.2.

*3 $^{13}C$ NMR spectrum: 18.41, 24.80, 37.51, 41.25, 49.59, 128.84, 131.28, 132.15, 137.05, 164.88, 169.38.

*4Here and in other cases, the coupling constants could not be measured due to the complex multiplicity of the signal.

*5 $^{13}C$ NMR spectrum: 38.82, 41.43, 48.43, 126.68, 127.82, 128.38, 129.34, 131.38, 131.53, 132.37, 132.62, 136.50, 168.27.

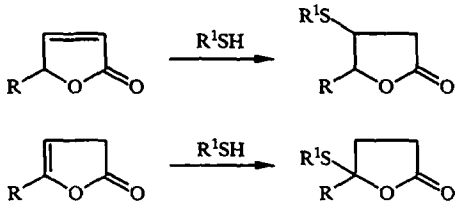
TABLE 5. Quantum Chemical Calculations of the Charges on $C_{(4)}$ ($Z_4$) of the Thione Form B of R-Substituted 2-Thiophenethiols I and Sulfur Atom ($Z_S$) of the Corresponding Thiolate Anion by the PM3, AM1, and MINDO/3 Methods

| R | PM3 | | AM1 | | MINDO/3 | |
|---|---|---|---|---|---|---|
| | $Z_4$ | $Z_S$ | $Z_4$ | $Z_S$ | $Z_4$ | $Z_S$ |
| 4-Me | -0,0624 | -0,5680 | -0,0656 | -0,5195 | 0,0774 | -0,7055 |
| H | -0,0918 | -0,5661 | -0,1302 | -0,5193 | 0,0707 | -0,7144 |
| 5-Me | -0,0958 | -0,5616 | -0,1303 | -0,5116 | 0,0648 | -0,7041 |
| 5-MeS | -0,1003 | -0,5118 | -0,1360 | -0,4651 | 0,0634 | -0,6764 |
| 3-Me | -0,1050 | -0,5588 | -0,1396 | -0,5085 | 0,0520 | -0,6957 |
| 5-Cl | -0,1167 | -0,5390 | -0,1415 | -0,4858 | | |
| 5-Ph | -0,0911 | -0,5174 | -0,1286 | -0,4481 | 0,0647 | -0,6877 |
| 3-Ph | -0,1118 | -0,5097 | -0,1272 | -0,4568 | 0,0410 | -0,6734 |
| 4-Ph | -0,0045 | -0,5517 | -0,0196 | -0,5000 | 0,0900 | -0,6934 |

How can this substituent effect be explained? What is the mechanism for self-thiylation?

Since the reactions of thiols with 5H- and 3H-2-furanones differ in their regioselectivity [17] (see Scheme 3),

Scheme 3




R = H, Me, Et; $R^1$ = Alk

we may assume by analogy that self-thiylation through Scheme 1 proceeds with the intermediate participation exclusively of tautomer B. Otherwise, we would expect formation of products of addition at $C_{(5)}$. In principle, this reaction could proceed through a radical, acid-catalyzed electrophilic, or base-catalyzed nucleophilic mechanism.

In the absence of catalyst, the self-thiylation of thiophenethiols probably proceeds through a radical mechanism. Indeed, samples of thiol Ia recondensed and stored in vacuum are stable for several weeks but convert to a mixture of dimer IIa and 2,2′-dithienyl sulfide [1] in only 24 h upon exposure to the air. There are, however, many examples of radical thiylation of α,β-unsaturated carbonyl compounds initiated by atmospheric oxygen [18].

The attack of the 2-thiophenethiyl radical probably can occur at both $C_{(4)}$ and the thiocarbonyl group, which leads to the corresponding 2,2′-dithienyl sulfides along with dimers IIa and IIb.

α,β-Unsaturated lactones also readily add thiols upon acid catalysis [17]. We did not carry out a systematic study of the reactivity of 2-thiophenethiol IIa under these conditions but repeatedly observed that decomposition of the mixture obtained in the preparation of 2-thiophenethiol IIa from 2-thienylmagnesium chloride and sulfur using excess HCl leads to rapid generation of hydrogen sulfide and a sharp drop in the yield of the desired thiol. Reaction at the thiocarbonyl fragment of tautomer B is probably also stimulated under acid catalysis conditions (see Scheme 4).

Scheme 4

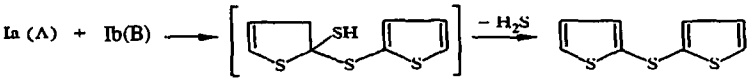


TABLE 6. Synthesis Methods and Indices of 2-(Trimethylsilylthio)thiophenes VII and VIIIa-f

| Compound | Name | Chemical formula | Found, % / Calculated, % | | | | Synthesis method * | bp, °C (mm Hg) [mp, °C] | $n_D^{23}$ | $M^+$, m/z, (%) | PMR spectrum, δ ppm, coupling constant (J, Hz) | | | | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | C | H | S | Si | | | | | 2-SSiMe3 S | 3-H(R) | 4-H(R) | 5-H(R) | |
| VII | 2,5-Bis(trimethylsilylthio)thiophene | $C_{10}H_{20}S_3Si_2$ | 40,72 / 41,05 | 6,73 / 6,89 | 34,07 / 32,87 | 18,48 / 19,20 | Na/HMDS [15] | 103(1) [23...25] | 1,5790 | 292(22) | 0,30 | 6,90 s | 6,90 s | 0,30 s ($Me_3SiS$) | 50 |
| VIIIa | 2-(Trimethylsilylthio)thiophene | $C_7H_{12}S_2Si$ | 44,16 / 44,63 | 6,47 / 6,42 | 33,68 / 34,04 | 14,75 / 14,91 | See Scheme 5 | 103(20) | | 188(23 | 0,29 | 6,90...7,02, $J_{34}$ = 3,4 m | 6,90...7,02 m | 7,20 d. d, $J_{35}$ =1,5, $J_{45}$ = 5,2 | 98 |
| VIIIb | 2-Trimethylsilylthio-3-bromothiophene | $C_7H_{11}BrS_2Si$ | 31,19 / 31,46 | 4,21 / 4,05 | 23,79 / 24,12 | 10,42 / 10,51 | PhLi/S/TMCS | 95(1,5) | 1,5753, $d_4^{23}$ = = 1,353 | 267(27) | 0,33 | | 6,96 d; $J_{45}$ = 5,6 | 7,19 d | 22 |
| VIIIc | 2-Trimethylsilylthio-3-methylthiophene | $C_8H_{14}S_2Si$ | 47,01 / 47,47 | 7,01 / 6,97 | 31,37 / 31,68 | 13,74 / 13,88 | Mg/S/$H^+$/HMDS [10] | 74...76 (5) | 1,5410 | 202(21) | 0,29 | 2,21 s (Me) | 6,84 d | 7,10 d | 12 |
| VIIId | 2-Trimethylsilylthio-4-methylthiophene | $C_8H_{14}S_2Si$ | 46,95 / 47,47 | 7,11 / 6,97 | 31,47 / 31,68 | 13,58 / 13,88 | PhLi/S/TMCS | 81(3,5) | | 202(23) | 0,30 | 6,77 m | 2,19 s (Me) | 6,77 m | 39 |
| VIIIe | 2-Trimethylsilylthio-5-methylthiophene | $C_8H_{14}S_3Si$ | 40,62 / 40,98 | 5,81 / 6,02 | 42,66 / 41,02 | 10,90 / 11,98 | PhLi/S/TMCS | 127(2) | | 234(16) | 0,30 | 6,89 d; $J_{34}$ = 3,7 | 6,97 d | 2,47 s (MeS) | 65 |
| VIIIf | 2-Trimethylsilylthio-5-trimethylsilylthiophene | $C_{10}H_{20}S_2Si_2$ | 45,96 / 46,10 | 7,61 / 7,74 | 25,49 / 24,61 | 20,46 / 21,56 | PhLi/S/TMCS | 82(2) [31,5] | | 260(14) | 0,29 | 7,04 d, $J_{34}$ = 3,4 | 6,98 d | 0,27 s ($Me_3Si$) | 63 |

*PhLi/S/TMCS) consecutive treatment of the corresponding thiophene by phenyllithium, sulfur, and trimethylchlorosilane [11, 12]; Mg/S/$H^+$/HMDS and Na/HMDS) as in indicated communications with subsequent heating of the organic extract after drying over $MgSO_4$ at reflux with excess hexamethyldisilazane.

On the other hand, in the presence of a catalytic amount of triethylamine, thiophenethiol Ia is converted to dimer IIa almost instantaneously and quantitatively. In this case, it is logical to presume that the reaction proceeds through a nucleophilic addition mechanism.

It is interesting to note that the reaction mixture turns bright pink upon the addition of triethylamine and after a few seconds, orange, which is characteristic for IIa. This effect probably has the following explanation. The transformation of form A of Ia into form B, similar to the tautomeric transformations of hydroxythiophenes, is a rather slow process, which is efficiently catalyzed by tertiary amines [7, 19]. In the absence of catalyst (under radical conditions), the rate-limiting step of the dimerization is formation of tautomer B. An equilibrium is immediately established between forms A, B, and C upon theaddition of triethylamine. Form B probably is pink due to the system of conjugated double bonds in this molecule. The relatively slow addition of tautomer A to tautomer B then occurs as the rate-limiting step under base catalysis conditions.

The appearance of the same pink color upon the vacuum distillation of thiophenethiol has been examined in our previous work [1]. Since samples of this compound always contain some amount of dimer IIa, distillation, especially in its final stages, involves thermal decomposition of this dimer to thiol Ia(A) and thione Ia(B). The high concentration of form B, which has not yet undergone tautomeric conversion, accounts for the observed color. Similar color effects were observed in a study on 2-thiopheneselenol [20, 21].

We attempted to detect the tautomeric thione forms B and C of Ia-p using PMR spectroscopy. Different solvents were used and the temperature was varied. Acid and base catalysts were added. Since 2-hydroxy-5-mercaptothiophene may potentially exist as its tautomeric dithiosuccinic anhydride derivative [22], we might have expected an enhanced content of thione forms also for 2,5-thiophenethiol Ij. However, all the compounds studied, Ia-p, proved to be pure thiols. This finding does not eliminate the possibility of participation of thione forms in the self-thiylation reactions, but only indicates their low concentration in the reaction mixtures below the PMR detection threshold [1, 4].

The literature data suggest that the effect of substituents at the double bond on the thiylation of $\alpha,\beta$-unsaturated carbonyl compounds under base catalysis conditions is analogous to the effect of substituents at $C_{(3)}$ and $C_{(4)}$ of the thiophene ring on the dimerization of 2-thiophenethiols. Thus, methyl methacrylate is thiylated much less readily than methyl acrylate [23], while the introduction of a methyl group at $C_{(3)}$ of the thiophene ring hinders self-thiylation of thiol If relative to its unsubstituted analog Ia. The methyl group at $C_{(4)}$ in Ig does not have a significant effect on the dimerization reaction. Analogously, ethyl acrylate and ethyl crotonate are thiylated with the same facility [24].

The inhibiting effect of the methyl group at $C_{(3)}$ apparently results from an increase in the charge on the carbon atom attacked due to a conjugation effect. This hypothesis is supported by semiempirical quantum chemical calculations (Table 5).

An explanation for the inhibiting effect of the Me and MeS groups at $C_{(5)}$, which also increase charge on the carbon atom but due to induction effects, is also found in the framework of this approach. Furthermore, a marked decrease in the negative charge on the attacking anion may also be noted for 5-methylthio derivative Ii.* Unfortunately, such simple considerations are inapplicable in the case of phenyl substituents, while the inertness of 4-phenyl-2-thiophenethiol in self-thiylation is not surprising since ethyl cinnamate is not thyilated under the same conditions as acrylates and crotonates [23, 24].

We obtained data on the inertness of 5-phenyl-2-thiophenethiol Im in self-thiylation reactions. However, Purcell et al. [16] described a four-step synthesis of 5-mercapto-2,2′-dithiophene In and reported that the "dimerization" of this compound was so facile that it was necessary to add triethylamine (probably in considerable molar excess [16, 25]) to the sample in order to take its PMR spectrum. Triethylamine facilitates conversion of the dimer to monomer. No indices of this dimer are given by Purcell et al. [16]. Since the phenyl and 2-thienyl substituents are extremely similar, these findings are clearly not in accord

*A good illustration of the different reactivities of 3- (If) and 4-methyl-2-thiophenethiols (Ig) is found in the formation of a derivative of the "mixed" dimer (IVp = IVf + IVg) upon reaction with phenylhydrazine. In this case, the dimer is not formed at all under competitive reaction conditions from thiol If

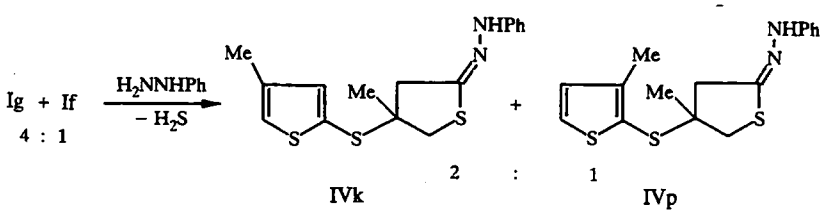


TABLE 7. Quantum Chemical Calculation of the Relative Stabilities of Tautomeric Forms A, B, and C of R-Substituted 2-Thiophenethiols I and Analogously Substituted Potential 2-Hydroxythiophenes IX*

| R | AM1 Calculation | | | | R | PM3 Calculation | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\Delta\Delta H_{B-C}$, kcal | | $\Delta\Delta H_{B-A}$, kcal | | | $\Delta\Delta H_{B-C}$, kcal | | $\Delta\Delta H_{B-A}$, kcal | |
| | IX | I | IX | I | | IX | I | IX | I |
| 3-Ph | -3,58 | -1,94 | 12,99 | -1,93 | 3-Me | -4,29 | -2,33 | 19,11 | 3,99 |
| 3-Me | -2,52 | -0,86 | 11,66 | -0,30 | 3-All | -4,65 | -2,22 | 19,01 | 2,98 |
| 3-All | -2,75 | -0,4 3 | 11,62 | 0,49 | 3-Ph | -2,52 | -2,02 | 21,99 | 2,75 |
| 3-Br | -2,11 | -0,34 | 13,39 | -3,47 | 3-Cl | -3,26 | -1,50 | 19,93 | 2,81 |
| 3-Cl | -1,63 | -0,02 | 13,28 | -2,59 | 4-Me | -0,10 | 2,33 | 17,74 | 4,64 |
| 4-Ph | 1,19 | 2,58 | 11,00 | -0,35 | 4-Ph | -0,29 | 2,52 | 17,86 | 5,06 |
| 4-Me | 0,93 | 2,80 | 10,42 | 0,29 | H | 0,17 | 2,53 | 18,49 | 4,10 |
| H | 1,04 | 2,97 | 11,08 | -0,31 | 4-Cl | 0,16 | 2,79 | 18,67 | 3,46 |
| 4-Cl | 1,48 | 3,52 | 11,57 | -1,23 | 3-Br | 3,52 | 4,99 | 19,98 | 2,59 |
| 5-Cl | 4,14 | 6,03 | 14,44 | -4,05 | 5-Cl | 3,81 | 6,01 | 22,17 | 1,32 |
| 5-Me | 4,43 | 6,23 | 14,14 | -3,29 | 5-Me | 4,38 | 6,62 | 22,31 | 1,10 |
| 5-Ph | 5,34 | 7,23 | 15,69 | -5,20 | 5-Ph | 4,59 | 6,79 | 23,02 | -0,41 |
| 5-SH | 7,73 | 8,65 | 18,21 | -8,28 | 5-SH | 5,67 | 9,12 | 24,68 | -1,65 |
| 5-MeS | 6,65 | 8,71 | 18,52 | -8,56 | 5-MeS | 5,65 | 9,21 | 25,29 | -3,07 |

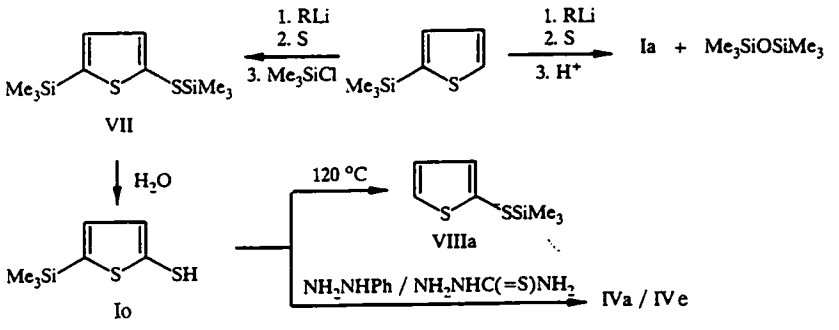
*The A, B, and C forms for IX are the hydroxy and oxo forms analogous to tautomeric forms A, B, and C for 2-thiophenethiol Ia.

with our results. We synthesized thiol In from 2,2'-dithienyl in one step according to the standard organolithium method and characterized it in detail (see Table 2). Our PMR spectral data for this compound are very similar to the parameters given by Purcell et al. [16] but, according to our data, thiol In, similar to its phenyl analog Im, is incapable of self-thiylation under the conditions studied (see Table 1). The reason for this discrepancy remains unclear. *

Different side-reactions may serve to account for the failure to obtain dimeric derivatives of thiols Ib-Id and Io. Thus, halothiols Ic and Id are unstable and spontaneously decompose with the release of HHal and $H_2S$ [6, 7, 8]. On the other hand, in the presence of a stoichiometric amount of triethylamine or phenylhydrazine, 5-chloro-2-thiophenethiol Id is converted into a mixture of disulfides [8]. Intramolecular cyclization and transallylation is favored over dimerization for 3-allyl-2- thiophenethiol Ib [9, 26, 27].

5-Trimethylsilyl-2-thiophenethiol Io was synthesized in quantitative yield only through its trimethylsilyl ether (VII) (see Table 6)† obtained by the action of an organolithium compound RLi and sulfur on 2-trimethylsilylthiophene; the yield of ether VII was 85% when R = Bu and 63% when R = Ph. Only 2-thiophenethiol Ia was obtained when standard methods were used involving decomposition of the reaction mixture by acid (see Scheme 5).

Scheme 5




*Flash chromatography on silica gel was used by Purcell et al. [16] to purify the desired thiol, while we used vacuum distillation.
†Thiols Ib [27] and Ic, If, Ii, and Ij were more conveniently prepared from the corresponding silyl ethers.

Thiol Io, which is stable at room temperature, quantitatively rearranges to give 2-(trimethylsilylthio)thiophene (VIIIa) in 3 h at 120°C. This reaction is probably intermolecular and may be termed "autocatalytic protodesilylation." The reaction of thiol Io with phenylhydrazine or thiosemicarbazide (in methanol at reflux) also proceeds with loss of the trimethylsilyl group but the phenylhydrazone IVa and thiosemicarbazone IVe of the dimeric form of unsubstituted 2-thiophenethiol IIa are formed, respectively, in this case. Small, rigid heteroarenechalcogen molecules are convenient models for quantum chemical investigations. We calculated the relative stabilities (RS) [28] of tautomeric forms B and C of substituted 2-hydroxy- (IX) and 2-mercaptothiophenes by the AM1 and PM3 methods. The calculation results shown in Table 7 indicate a definite preference for the thiol form in the case of 2-thiophenetihols and similar $\Delta H$ values for the formation of all three tautomeric forms in the case of 2-hydroxythiophenes, which corresponded to the experimental data [7]. The effect of substituents on the RS for hydroxy- and mercaptothiophenes is identical and in complete qualitative accord with the empirical data obtained for hydroxythiophenes: substituents at $C_{(3)}$ and $C_{(4)}$ stabilize form B, while substituents at $C_{(5)}$ stabilize form C.

## EXPERIMENTAL

The NMR spectra were taken for $CDCl_3$ solutions (the spectra of IVb, IVc, IVg-IVj, IVm, and VI were taken in deuteroacetone) on a Varian VXR-500 spectrometer at 500 MHz or Bruker WP-200 SY spectrometer at 200 MHz. The GC/MS were taken on an LKB-2091 instrument at 70 eV using a 25-m SE-30 column with temperature programming from 135 to 240°C (8 deg/min) or with direct sample inlet (IIb, IVb, IVc, IVg-IVi, V, and VI).

The quantum chemical calculations were carried out on an IBM PC 486 DX4-100 using the MOPAC 6.0 program. PC Model 3.2 was used to introduce the structures and perform their initial optimization. Complete optimization of the geometry was carried out by the same method as for calculation of the electronic structure.

Starting 3-methyl, 2- and 3-phenylthiophenes, and 2,2′-dithienyl for the synthesis of thiols Ik-n were obtained by the Grignard–Wurtz reaction using $NiCl_2$(dppp) as the catalyst [29].

A sample of 2-*tert*-butylthiophene for the synthesis of thiol Ip was kindly provided by L. I. Belen'kii.

A sample of γ-dithiobutyrolactone was synthesized in 17% yield by heating γ-butyrolactone with a two-fold excess of $P_2S_5$ in dioxane.

2-Thiophenethiol Ia was obtained from 2-thienylmagnesium chloride and sulfur using a modification of our previous procedure [1] (the organic layer was additionally extracted with aqueous alkali and reacidified and all the operations were carried out in an argon atmosphere) to increase the yield to 89% (vs. only 45% in our previous work [1]). Thiols Ib-p were prepared using standard organometallic methods (see references in Table 4) or, as described in our previous work [11, 12, 20], by hydrolysis of the corresponding trimethylsilyl ethers (Table 5).

"Dimer" IIb spontaneously formed from thiol Ig upon standing. Hydrazones IVb, IVc, IVg, IVh, and IVk-o were obtained by heating a mixture of the corresponding thiol and hydrazine in 2:1 mole ratio (without solvent) until $H_2S$ was no longer released (see Table 1 and our previous work [5]) and studied without further purification. Product VI was similarly obtained.

Azines IIIa and V, 2,4-dinitrophenylhydrazone IVd, benzoylhydrazone IVf, thiosemicarbazones IVe and IVj, and oxime IVi were obtained by heating thiol Ia or γ-dithiobutyrolactone with an equimolar amount of the corresponding hydrazine, thiosemicarbazide, or hydroxylamine in methanol at reflux until $H_2S$ was no longer liberated (3-4 h, 48 h for IVd) and further recrystallized from methanol—tetrahydrofuran (see Tables 3 and 4).

This work was carried out with the financial support of the Russian Basic Research Fund (Grant 94-03-08837).

## REFERENCES

1. V. Yu. Vvedenskii, S. V. Zinchenko, T. A. Shkarupa, N. A. Korchevin, É. N. Deryagina, and M. G. Voronkov, Dokl. Akad. Nauk SSSR, **305**, 624 (1989).
2. G. S. Ponticello, C. N. Habecker, S. L. Varga, and S. M. Pitzenberger, J. Org. Chem., **54**, 3223 (1989).
3. M. V. Ul'yev, E. D. Shtefan, and V. Yu. Vvedenskii, Usp. Khim., **60**, 2528 (1991).
4. E. D. Shtefan and V. Yu. Vvedenskii, Usp. Khim., **65**, 326 (1996).

5. V. Yu. Vvedenskii, T. A. Shkarupa, S. V. Zinchenko, A. R. Zhnikin, É. N. Deryagina, and M. G. Voronkov, Zh. Org. Khim., **26**, 2237 (1990).
6. E. Jones and I. M. Moodie, Tetrahedron, **21**, 1333 (1965).
7. S. Gronowitz (ed.), Thiophene and Its Derivatives, Part 3, Interscience Publ., New York (1986), Ch. 1, p. 40.
8. V. Yu. Vvedenskii, E. D. Shtefan, M. V. Ul'yev, A. R. Zhnikin, T. A. Shkarupa, É. N. Deryagina, and M. G. Voronkov, Zh. Org. Khim., **28**, 212 (1992).
9. A. V. Anisimov, V. F. Ionova, and V. A. Viktorova, Khim. Geterotsikl. Soedin., No. 2, 186 (1978).
10. S. Gronowitz, P. Mozes, and A.-B. Hornfeldt, Ark. Kemi, **17**, 237 (1961).
11. V. Yu. Vvedenskii [Vvedensky], E. D. Shtefan, M. V. Ul'yev [Ulyev], É. N. Deryagina [E. N. Deryagina], and M. G. Voronkov, Sulfur Lett., **17**, 257 (1994).
12. V. Yu. Vvedenskii, E. D. Shtefan, R. N. Malyushenko, and É. N. Deryagina, Khim. Geterotsikl. Soedin., No. 7, 891 (1994).
13. Ya. L. Gol'dfarb, M. A. Kalik, and M. L. Kirmalova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 1696 (1960).
14. S. Gronowitz and R. A. Hoffman, Ark. Kemi, **15**, 499 (1960).
15. Ya. L. Gol'dfarb and M. A. Kalik, Khim. Geterotsikl. Soedin., No. 5, 788 (1968).
16. S. T. Purcell, N. Garcia, V. T. Binh, L. Jones, and J. M. Tour, J. Am. Chem. Soc., **116**, 11985 (1994).
17. S. Ducher and A. Michet, Bull. Soc. Chim. France, No. 3 (Part 2), 1037 (1973).
18. E. N. Prilezhaeva and M. F. Shostakovskii, Usp. Khim., **32**, 897 (1963).
19. S. Gronowitz, Khim. Geterotsikl. Soedin., Nos. 11/12, 1445 (1994).
20. V. Yu. Vvedenskii, S. V. Zinchenko, E. D. Shtefan, M. V. Ul'yev, A. R. Zhnikin, T. A. Shkarupa, and É. N. Deryagina, Dokl. Akad. Nauk SSSR, **320**, 96 (1991).
21. V. Yu. Vvedenskii [Vvedensky], S. V. Zinchenko, E. D. Shtefan, M. V. Ul'yev [Ulyev], A. R. Zhnikin, T. A. Shkarupa, and É. N. Deryagina [E. N. Deryagina], Sulfur Lett., **14**, 129 (1992).
22. H. J. Jakobsen, E. N. Larsen, and S.-O. Lawesson, Tetrahedron, **19**, 1867 (1963).
23. L. L. Gershbein and C. D. Hurd, J. Am. Chem. Soc., **69**, 241 (1947).
24. K. Ruhlmann, D. Heuchel, U. Schrapler, and D. Gramer, J. Prakt. Chem., **11**, 40 (1960).
25. J. M. Tour, L. R. Jones II, D. L. Pearson, J. J. S. Lamba, T. P. Burgin, G. M. Whitesides, D. L. Allara, A. N. Parikh, and S. V. Atre, J. Am. Chem. Soc., **117**, 9529 (1995).
26. A. V. Anisimov, E. A. Viktorova, and T. A. Danilova, Molecular Rearrangements of Organosulfur Compounds [in Russian], Izd. Moskovsk. Gos. Univ., Moscow (1989), p. 67.
27. V. Yu. Vvedenskii [Vvedensky], E. D. Shtefan, R. N. Malyushenko, and É. N. Deryagina [E. N. Deryagina], Sulfur Lett., **18(4)**, 173 (1995).
28. A. R. Katritzky, M. Szafran, and J. Stevens, J. Mol. Struct. (Theochem), **184**, 179 (1989).
29. K. Tamao, S. Kodama, I. Nakajima, M. Kumada, A. Minato, and K. Suzuki, Tetrahedron, **38**, 3347 (1982).