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SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences B.A. Trofimov on the 65th Anniversary of His Birth

Reactions of Thiophene-2-carbaldehydes with Thiols in the Presence of Chlorotrimethylsilane

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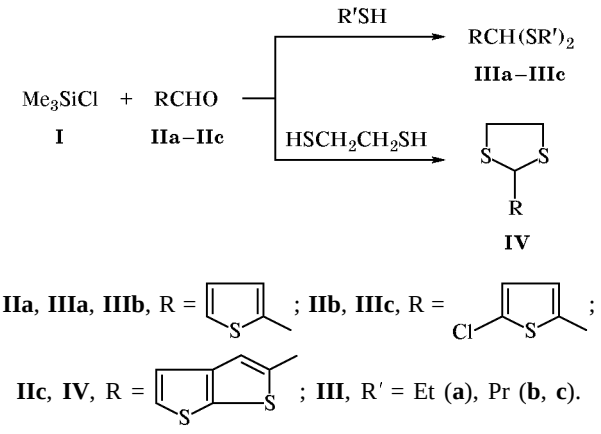
The system aliphatic aldehyde–chloro(trimethyl)-silane (**I**) is effective in the chloroalkylation of alkanethiols. Paraformaldehyde reacts with alkanethiols at –5 to 0°C in a large excess of silane **I** to give mainly alkyl chloromethyl sulfides. The latter are capable of reacting with alkanethiols with formation of thioacetals in no more than 30% yield [1]. Under similar conditions, the reaction of isobutyraldehyde with alkanethiols leads to formation of vinyl sulfides as the major products (yield 55–72%) as a result of dehydrochlorination of intermediate alkyl chloroalkyl sulfides; here, thioacetals are formed in small amounts (8–39%) [2].

We have found that aldehydes **IIa**–**IIc** of the thiophene series react with the system alkanethiol–chloro-(trimethyl)silane in a different way. By reactions of ethanethiol, 1-propanethiol, and 1,2-ethanedithiol with an equimolar amount of aldehyde **IIa**–**IIc** in 4–8-fold excess of silane **I** we obtained previously unknown thioacetals **IIIa**–**IIIc** and **IV**. The reaction with 1,2-ethanedithiol was accompanied by a strong exothermic effect. Acyclic and cyclic dithioacetals **III** and **IV** were the only reaction products (yield 56–90%). In the absence of silane **I**, the yields were much lower (8–15%). The structure of compounds **III** and **IV** was confirmed by elemental analyses, ^{1}H and ^{13}C NMR spectra, and mass spectra. The products attract interest as potential biologically active substances [3] and synthons [4, 5].



IIa, **IIIa**, **IIIb**, R = ; **IIb**, **IIIc**, R = ;

IIc, **IV**, R = ; **III**, R′ = Et (**a**), Pr (**b**, **c**).

2-[Bis(ethylsulfanyl)methyl]thiophene (IIIa). Ethanethiol, 3.04 g (0.04 mol), was added dropwise at –5°C to a mixture of 2.24 g (0.02 mol) of aldehyde **IIa** and 20 ml of chloro(trimethyl)silane (**I**). The mixture was vigorously stirred for 1.5 h at –8 to –5°C and was allowed to warm up to room temperature. The progress of the reaction was monitored by GLC. After removal of silane **I**, the product was isolated by vacuum distillation. Yield 3.3 g (68%), light yellow oily substance, bp 132–135°C (1–2 mm). ^{1}H NMR spectrum, δ, ppm: 1.22 t (3H, CH_3), 2.59 d.q (2H, SCH_2, part *A* of *AB* quartet, ^2J = 12.72 Hz, ^3J = 7.46 Hz), 2.66 d.q (2H, SCH_2, part *B* of *AB* quartet), 5.21 s (1H, CH); thiophene ring: 6.88 d.d (1H, 4-H, $^3J_{4,3}$ = 3.55 Hz, $^3J_{4,5}$ = 5.14 Hz), 7.06 d.d.d (1H, 3-H, $^4J_{3,SCHS}$ = 0.74 Hz), 7.20 d.d (1H, 5-H, $^4J_{5,3}$ = 1.34 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.02 (CH_3), 25.91 (SCH_2), 47.43 (CH); thiophene ring: 125.19 (C^3), 125.51 (C^4), 126.19 (C^5), 144.31 (C^2). Found, %: C 49.88; H 6.48; S 43.33. M^+ 218. $C_9H_{14}S_3$. Calculated, %: C 49.54; H 6.42; S 44.03. *M* 218.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

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2-[Bis(propylsulfanyl)methyl]thiophene (IIIb). Yield 70.4%, bp 135–136°C (1–2 mm), n_D^{20} = 1.5625. ^{1}H NMR spectrum, δ, ppm: 0.95 t (3H, CH_3), 1.59 s (2H, CH_2, ^3J = 7.4 Hz), 2.54 d.t (2H, SCH_2, part *A* of *AB* quartet, ^2J = 12.72 Hz, ^3J = 7.46 Hz), 2.63 d.t (2H, SCH_2, part *B* of *AB* quartet), 5.16 s (1H, CH); thiophene ring: 6.88 d.d (1H, 4-H, $^3J_{4,3}$ = 3.55 Hz, $^3J_{4,5}$ = 4.89 Hz), 7.06 d.d.d (1H, 3-H, $^4J_{3,SCHS}$ = 0.74 Hz), 7.19 d.d (1H, 5-H, $^4J_{5,3}$ = 1.34 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.54 (CH_3), 22.48 (CH_2), 34.13 (CH_2S), 48.30 (CH); thiophene ring: 125.29 (C^3), 125.65 (C^4), 126.33 (C^5), 145.31 (C^2). Found, %: C 54.33; H 5.06; S 38.93. M^+ 246. $C_{11}H_{18}S_3$. Calculated, %: C 53.93; H 7.31; S 39.0. *M* 246.

2-Chloro-5-[bis(propylsulfanyl)methyl]thiophene (IIIc). Yield 56.2%, bp 165–170°C (2–3 mm), n_D^{20} = 1.5748. ^{1}H NMR spectrum, δ, ppm: 0.96 t (3H, CH_3, ^3J = 7.21 Hz), 1.58 s (2H, CH_2), 2.54 d.t (2H, SCH_2, part *A* of *AB*-quartet, ^2J = 12.6 Hz), 2.63 d.t (2H, SCH_2, part *B* of *AB* quartet), 5.02 s (1H, CH); thiophene ring: 6.68 d (1H, 4-H, $^3J_{4,3}$ = 3.67 Hz), 6.83 d (1H, 3-H). ^{13}C NMR spectrum, δ_C, ppm: 13.50 (CH_3), 22.42 (CH_2), 34.11 (CH_2S), 48.60 (CH); thiophene ring: 125.01 (C^3), 125.45 (C^4), 129.85 (C^5), 144.37 (C^2). Found, %: Cl 13.0; S 34.85. $C_{11}H_{17}ClS_3$. Calculated, %: Cl 12.65; S 34.29.

2-(1,3-Dithiolan-2-yl)thieno[2,3-*b*]thiophene (IV). 1,2-Ethanedithiol, 1.41 g (0.015 mol), was added dropwise at 0°C to a mixture of 2.52 g (0.015 mol) of aldehyde **IIc** and 8 ml (0.063 mol) of silane **I**. The reaction was accompanied by strong heat evolution; therefore, 1,2-ethanedithiol was added slowly. The mixture was vigorously stirred for 1.5 h at –5 to 0°C and was allowed to warm up to room temperature. The precipitate was filtered off, recrystallized thrice from benzene–ethanol (1 : 2), and dried under reduced pressure. Yield 3.3 g (90%), light pink crystals, mp 81–83°C. ^{1}H NMR spectrum, δ, ppm: 3.29 m and 3.44 m (4H, SCH_2CH_2S), 5.90 s (1H, CH); thieno-[2,3-*b*]thiophene system: 7.07 d (1H, 5-H, $^3J_{5,6}$ = 5.2 Hz), 7.17 s (1H, 3-H), 7.24 d (1H, 6-H). ^{13}C NMR spectrum, δ_C, ppm: 39.95 (SCH_2), 51.67 (CH); thieno-[2,3-*b*]thiophene system: 118.32 (C^3), 119.92 (C^5), 127.42 (C^6), 137.34 (C^4), 145.64 (C^2), 150.32 (C^7). Found, %: C 45.16; H 3.56; S 51.94. M^+ 244. $C_9H_8S_4$. Calculated, %: C 44.26; H 3.27; S 52.45. *M* 244.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 400.1 and 100.6 MHz, respectively; $CDCl_3$ was used as solvent, and HMDS, as internal reference. The mass spectra (electron impact, 57 eV) were run on an LKB-2091 instrument.

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