Dithio and Thiono Esters, 62[◇]

Reactions of Alkanedithioic Acid Dianions with Iodine, Sulfur, and Tin Compounds☆

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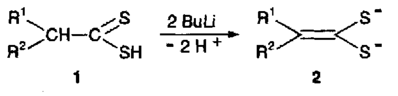
The monoanion of the alkanedithioic acid **1a** is oxidized with hypervalent iodine compounds to form the 1,2-dithiine **6**, the monoanion of **1b** yields the 1,2,4-trithiolane **7** and the dianions **2b**, **c** furnish the 1,2,4,5-tetrathianes **3b**, **c**. With diphenyltin or dimethyltin dichlorides **8** the monoanions of **1b**, **c** afford the monothioacyl or bisthioacyl organotin sulfides **10a–c** or **11a**, **b** respectively. When treated with lithium hexamethyldisilazane, **10b** undergoes an intramolecular cyclization to the 1,3,2-dithiastannetane **9b**; **10a** is deprotonated by triethylamine to the 1,3,5-trithia-2-stanninane **13**. The dianion **2c** reacts with diphenyltin dichloride **8** to yield the 1,3,2-dithiastannetane **9d**, with dimethyltin dichloride the 1,2,4-trithiolane **16** is formed. **9d** is cleaved by thionyl chloride, sulfur dichloride, and disulfur dichloride to give a complex mixture of the 1,2,4,5-tetrathiane **3c** and the cyclic polysulfides 1,2,3,4,5,6-hexathiepane **18**, 1,2,3,5,6,7-hexathiocane **19** and the 1,2,3,5,6-pentathiepane **20** in varying amounts. Reaction of the dianion **2b** with thionyl chloride leads to the formation of the 1,2,4,5-tetrathiane **3b** as main product; byproducts are cyclic polysulfides, the 1,2,3,5,6-pentathiepane **21** and the 1,2,3,4,5,6-hexathiepane **22**.

Alkanedithioic acids **1** with at least one hydrogen atom at the α carbon are readily deprotonated by strong bases to the corresponding dianions **2**. In most cases commercially available *n*-butyllithium can be used as a base. Chemical reactions of the dianions **2** have hardly been studied so far. In a previous paper we described the addition of **2** to carbon disulfide[1]. Here we report on further reactions of **2** with organic and inorganic compounds of iodine, sulfur, and tin[2].

Scheme 1



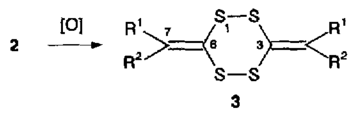
1, 2	R¹	R²
a	Me	H
b	Me	Me
c	Ph	Ph

Reactions with Hypervalent Iodine Compounds

Monoanions of dithio acids and enthiolates of dithio esters have normally been oxidized by elemental iodine or hexacyanoferrates(III). The products formed were open chain or cyclic organothiacyl disulfanes or α,β-unsaturated disulfanes[3]; sulfur heterocycles such as dithietanes[4] and 1,2,4-trithiolanes[5,6] were also isolated. Oxidation reactions of dithioacids dianions have not been studied so far.

α,α-Disubstituted species such as **2b** and **2c** react with [bis(trifluoroacetoxy)iodo]benzene[7] to give the expected 1,2,4,5-tetrathianes **3b**, **c** in moderate yield. α-Monosubstituted species such as **2a** were only converted to a complex mixture of decomposition products. The structure of **3** is based on analytical and spectroscopic data. The quaternary carbon atoms C-6 and C-7 show a difference in chemical shift of about 10 ppm in the ^{13}C-NMR spectra. The lower field signal was assigned to C-7 due to an observed coupling (^3J = 3.8 Hz) between the ortho protons of the phenyl ring and C-7 in a ^{13}C-,^{1}H-gated decoupled NMR spectrum of **3c**. **3b** and **3c** were also obtained in reactions of the corresponding dianions with thionyl chloride; in addition, **3c** is also accessible with disulfur dichloride.

Scheme 2



3	R¹	R²	yield [%]
a	Me	H	-
b	Me	Me	35
c	Ph	Ph	51

Up to now only a few 1,2,4,5-tetrathianes of type **3** have been described in the literature, R¹ and R² representing electronegative substituents[5,6,8] or cycloalkyl groups[9].

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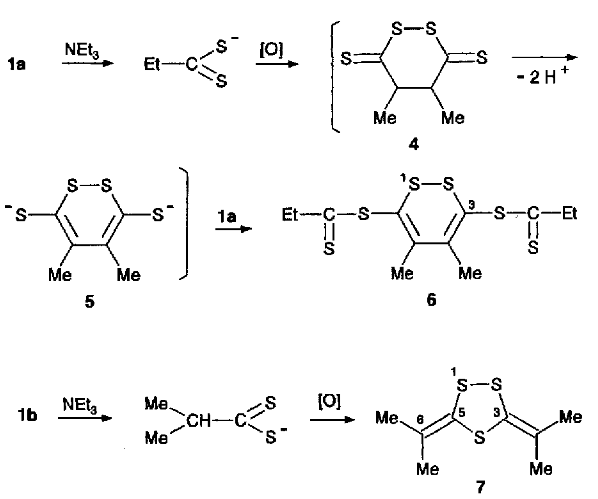
They were prepared by different routes. Schönberg, Frese, and Brosowski isolated **3c** from a reaction of diphenyl diazomethane with carbon disulfide in 64% yield[10].

The monoanion of dithiopropanoic acid (**1a**), formed in situ with triethylamine, is oxidized by hypervalent iodine compounds to the 1,2-dithiin **6**, isolated as red oil. The yields were rather low: with (dichloro)iodobenzene 14% of pure product were obtained, with [bis(acetoxy)iodo]benzene 20%. The first steps of the complex reaction sequence are most probably oxidations at the sulfur and at the α carbon atoms leading to an intermediate such as **4**, which is deprotonated twice to **5** and then thioacylated to form **6**. 1,2-Dithiins have attracted considerable attention in recent years[11]. The parent heterocycle tends to eliminate readily sulfur; substituted derivatives are generally stable at room temperature.

The monoanion of 2-methyl-dithiopropanoic acid (**1b**) is oxidized by [bis(acetoxy)iodo]benzene to the known 1,2,4-trithiolane **7** (15% yield)[12,13,14].

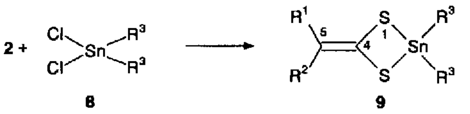
Scheme 3



Reactions with Organotin Chlorides

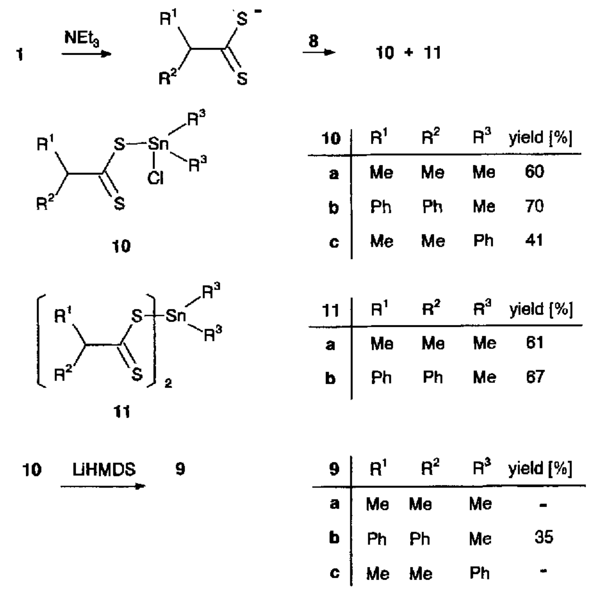
Reactions of dithioacids with organotin chlorides lead to organotin thioacetylthiolates. The older literature is summarized in ref.[15], more recent studies were reported by Kato and coworkers[16]. We expected to obtain 1,3,2-dithiastannetanes **9** by the reaction of dithioacid dianions **2** with organotin dichlorides **8**. The preliminary experiments, however, led to a complex mixture of products. Therefore, a stepwise approach was initiated.

Scheme 4



The dithioacids **1** were deprotonated in situ by triethylamine to the corresponding monoanions and then treated with the organotin dichlorides **8**. Depending on the molar ratio of the starting compounds, either the monothiacyl or bisthioacyl organotin sulfides (**10** or **11**, respectively) were isolated. **10** and **11** are perfectly stable at room temperature. According to the signals of the thiocarbonyl groups in the ^{13}C-NMR spectra (e.g. **10a**: δ = 265.2, **11a**: δ = 261.9) there is no interaction between sulfur and tin.

Scheme 5



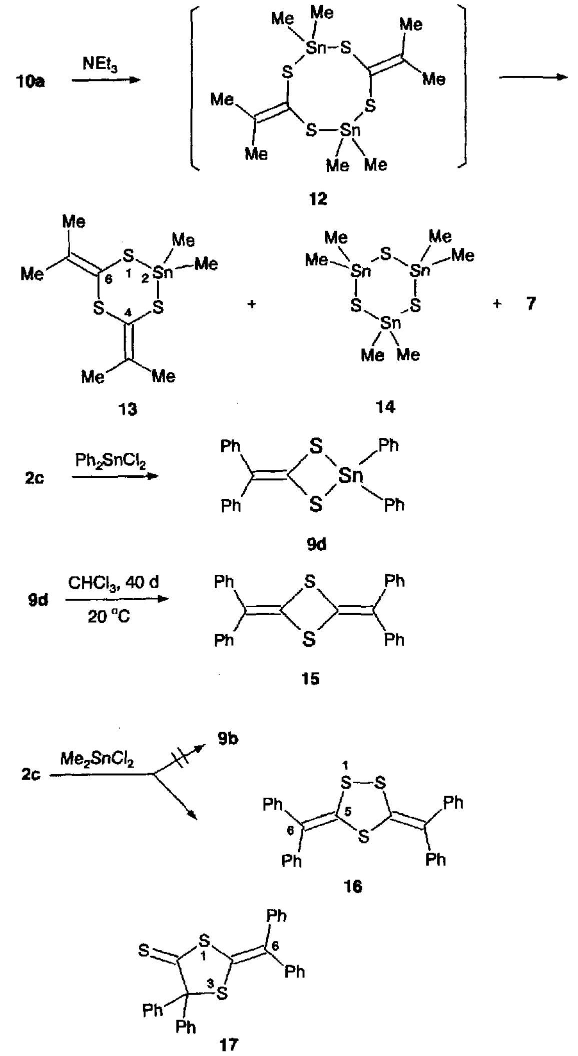
10	R1	R2	R3	yield [%]
a	Me	Me	Me	60
b	Ph	Ph	Me	70
c	Me	Me	Ph	41

11	R1	R2	R3	yield [%]
a	Me	Me	Me	61
b	Ph	Ph	Me	67

9	R1	R2	R3	yield [%]
a	Me	Me	Me	-
b	Ph	Ph	Me	35
c	Me	Me	Ph	-

A deprotonation of **10** at the carbon atom α to the thiocarbonyl group should lead to the 1,3,2-dithiastannetanes **9**. This reaction could be realized with **10b** and lithium hexamethyldisilazane (LiHMDS) leading to **9b** in 35% yield. A similar reaction was observed with **10c**. In the crude reaction mixture **9c** could be detected by its NMR signals. Due to its instability, however, the isolation of an analytical pure sample failed. By chromatography on silica gel only decomposition products [e.g. trimeric diphenyltin sulfide (28%) and the 1,2,4-trithiolane **7** (7%)] could be isolated. **10a** and LiHMDS gave a mixture of products similar to that obtained from the dianion **2b** and dimethyltin dichloride **8** (R^3 = Me). The course of this reaction was partially elucidated by treatment of **10a** with triethylamine leading to the formation of the 1,3,5-trithia-2-stanninane **13**, 1,3,5-trithia-tristannane **14**, and traces of the 1,2,4-trithiolane **7**. We suppose, that the monoanion obtained by deprotonation of **10a** does not cyclize intramolecularly to a 4-membered ring but rather intermolecularly to the 8-membered ring **12**. **12** is unstable and eliminates dimethyltin sulfide leaving behind the 6-membered 1,3,5-trithia-2-stannane **13**, whereas dimethyltin sulfide trimerizes to the more stable **14**. Due to the instability of **13**, a clean separation of **13** and **14** by column chromatography could not be achieved. Nevertheless, the proposed structure **13** was supported by the NMR data and high-resolution mass spectroscopy. A small amount of **13** (ca. 7%) could also be isolated from the reaction of the dianion **2b** with dimethyltin dichloride.

Scheme 6



The experiments described so far indicate, that stable 1,3,2-dithiastannetanes **9** should bear phenyl groups as substituents, at least at the exocyclic C-5. Thus, the condensation of 2,2-diphenyldithioethanoic acid dianion (**2c**) with diphenyltin dichloride **8** (R^3 = Ph) lead directly to the 1,3,2-dithiastannetane **9d** in 78% yield. The same dianion **2c**, however, does not condense with dimethyltin dichloride **8** ($R^3 = CH_3$) to form the expected 1,3,2-dithiastannetane **9b**. Instead of **9b** the known 1,2,4-trithiolane **16** (21% yield) was isolated. Higher yields of **16** (55%) were achieved by deprotonation of **11b** with LiHMDS followed by oxidation with iodine. **16** is also formed in the reaction of 2,2-diphenyldithioethanoic acid dianion (**2c**) with sulfur (38% yield); as a byproduct the 1,3-dithiolane-5-thione **17** (5% yield) was isolated.

The molecular mass of the crystalline 1,3,2-dithiastannetane **9d** was confirmed by a mass spectrum with field-desorption technique. The compound remains unchanged for weeks in the refrigerator. In solution at room temperature, however, **9d** is slowly transformed into the 1,3-dithietane **15**. We suppose that **9d** dissoziates primarily into diphenylthioketene and diphenyltin sulfide.

Reactions with Inorganic Sulfur Compounds

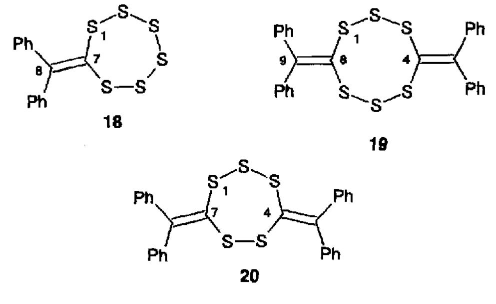
The unstable 1,3,2-dithiastannetane **9d** should be cleaved readily by reactive halogen reagents such as XCl_2. This was confirmed by experiments with thionyl chloride, sulfur dichloride and disulfur dichloride affording a complex mixture of products. The main components could be separated and purified by careful chromatography. With the dianion **2c** of 2,2-diphenyldithioethanoic acid and the same sulfur reagents comparable mixtures of products were obtained, however, in lower total yields.

The 1,2,4,5-tetrathiane **3c** is the main cleavage product of **9d** with thionyl chloride, accompanied by small amounts of the cyclic polysulfides **18** and **20**. After treatment of **9d** with both sulfur chlorides, SCl_2 and S_2Cl_2, only cyclic polysulfides such as the 1,2,3,4,5,6-hexathiepane **18**, the 1,2,3,5,6,7-hexathiocane **19** and the 1,2,3,5,6-pentathiepane **20** were isolated from the complex reaction mixture. Byproducts are probably related cyclic polysulfides with even more sulfur atoms in their rings and polymeric material. The structure of **17**–**19** is mainly based on the results of the elemental analyses and mass-spectroscopic data including field-desorption techniques. The ^{13}C-NMR spectra of **3c**, **18**, and **19** display only one set of signals of phenyl carbon atoms, whereas that of the less symmetrical **20** exhibits two sets of signals of the phenyl carbon atoms. The pentathiepane **20** is unstable; it eliminates sulfur giving rise to the formating of tetrathiane **3c**, the NMR signals of which could be detected in a $CDCl_3$ solution after standing at room temperature for a few days. In contrast to **20** the hexathiepane **18** is stable for months.

Scheme 7

$$\mathbf{9d} \xrightarrow{XCl_2} \mathbf{3c} + \mathbf{18} + \mathbf{19} + \mathbf{20}$$

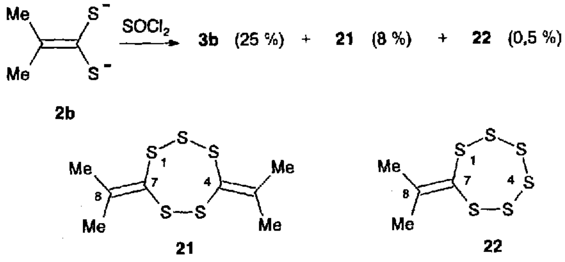
	yield [%]			
XCl_2	3c	18	19	20
$SOCl_2$	23	7	-	2
SCl_2	-	12	10	6
S_2Cl_2	-	16	4	4



Cyclic polysulfides have attracted considerable attention in recent years. They were not only synthesized in laboratory[17] but are also found in nature[18]. A prominent example is the cyclic pentasulfide varacain with a benzopentathiepin ring, isolated from marine organisms, showing potent antifungal and antitumor activity[18b].

When the dianion **2b** of 2-methyldithiopropanoic acid was treated with thionyl chloride, the 1,2,4,5-tetrathiane **3b** could be isolated in 25% yield; byproducts were the cyclic polysulfides 1,2,3,5,6-pentathiepane **21** and 1,2,3,4,5,6-hexathiepane **22**.

Scheme 8



The reaction products of the dianion **2a** of dithiopropanoic acid with the sulfur reagents discussed were so unstable, that they decomposed during chromatographic work-up procedures.

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Experimental

NMR (TMS as internal standard): Jeol JNM-FX 100 (probe temperature 25 °C); Jeol JNM-GX 400 (25 °C). – MS (70 eV): Vacuum Generators 70/70. – FD-MS (field desorption MS): MAT 711 Varian. The mass data refer to the isotopes ^{120}Sn, ^{35}Cl, and ^{32}S. – Melting points (uncorrected): Leitz heating microscope HM-Lux. – 2,2-Diphenyldithioethanoic acid (**1c**), first described by Schönberg and coworkers[19] was prepared as indicated below. **1a**, **b** were synthesized by a general procedure described in ref.[1] **1a** was stored at −30 °C as a solution in THF (2 M); **1b**, **c** are stable in crystalline form at −30 °C.

2,2-Diphenylethanedithioic Acid (**1c**): To a stirred solution of diphenylmethane (16.82 g, 0.1 mol) in dry THF (150 ml) BuLi (1.6 M in hexane, 6.33 ml, 0.105 mol) is added dropwise at −20 °C under N_2. After 2 h at −5 °C and 3 h at room temp. the solution is cooled again to −20 °C and treated with a solution of CS_2 (6.33 ml, 0.105 mol) in 20 ml of THF. Stirring is continued at −20 °C for 30 min and at room temp. for 20 h. Then the reaction mixture is shaken at 0 °C with petroleum ether (30 ml) and HCl (10%, 50 ml). The aqueous phase is extracted several times with diethyl ether/petroleum ether. The combined organic phases are washed with 30 ml of water and extracted several times at 0 °C with aqueous NH_3 (10%) until the organic layer is colorless. The combined NH_3 phases are washed with diethyl ether/petroleum ether. Then they are shaken in the presence of diethyl ether/petroleum ether (30 ml) with ice cooling with sufficient aqueous HCl (10%) until the aqueous phase is colorless. The latter is extracted several times with diethyl ether/petroleum ether, the combined organic layers are washed with water, dried with Na_2SO_4 and concentrated in vacuo. The residue, a dark red oil (20.8 g, 85% yield), crystallizes by the addition of a small amount of hexane: orange red crystals, m.p. 30 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.24 (10H, m, aromat. H), 6.0–6.3 (1H, s, SH), 5.74 (1H, s, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 237.5 (C=S), 140.1 (C-1′), 128.89, 128.50 (C-2′, -3′, -5′, -6′), 127.5 (C-4′), 72.6 (C-2). – $C_{14}H_{12}S_2$ (244.4): calcd. C 68.81, H 4.95, S 26.24; found C 68.55, H 4.99, S 26.17.

3,6-Diisopropylidene-1,2,4,5-tetrathiane (**3b**): a) To a stirred solution of BuLi (1.6 M in hexane, 6.25 ml, 10 mmol) in dry THF (20 ml), a solution of 2-methylpropanedithioic acid (**1b**, 0.60 g, 5 mmol) in 5 ml of THF is added dropwise at −78 °C under N_2. After 30 min at this temp. and 1.5 h at −5 °C the solution of the formed dianion **2b** has become nearly colorless. It is then cooled to −50 °C and treated dropwise with a solution of [bis(trifluoroacetoxy)iodo]benzene (4.3 g, 10 mmol) in 20 ml of THF. After 30 min the reaction mixture is allowed to warm to room temp. and stirring is continued for 3 h. Then $CHCl_3$ (30 ml) and water (30 ml) are added and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are dried with Na_2SO_4 and concentrated in vacuo. The oily residue solidifies by the addition of hexane affording 205 mg (35%) of yellow crystals; m.p. 165–172 °C (from hexane/ethyl acetate).

b) To a stirred solution of the dianion **2b** (10 mmol) (prepared as described under a), thionyl chloride (0.80 ml, 11 mmol) is added dropwise at −100 °C under N_2. Stirring is continued at −100 to −70 °C for 45 min and at −20 to 0 °C for 3 h. Then at this temp. $CHCl_3$ (30 ml) and water (30 ml) are added and the mixture is worked up (as described under a). The orange brown residue is purified on silica gel with cyclohexane to furnish as second fraction 300 mg (25%) of yellow needles; m.p. 165–172 °C. Byproducts are **21** (8%, third fraction) and **22** (0.5%, first fraction). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.99 (s, CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6 (C-7), 126.1 (C-3, -6), 23.1 (CH_3). – MS; *m*/*z* (%): 236 (32) [M^+], 204 (3), 150 (33), 86 (100). – $C_8H_{12}S_4$ (236.4): calcd. C 40.64, H 5.12, S 54.25; found C 40.40, H 4.88, S 54.44.

3,6-Bis(diphenylmethylene)-1,2,4,5-tetrathiane (**3c**): a) To a stirred solution of the dianion **2c** in dry THF – prepared from 2,2-diphenylethanedithioic acid (**1c**, 1.22 g, 5 mmol) and BuLi (1.6 M in hexane, 6.25 ml) as described for the dianion **2b** (under **3b**, method a) – a solution of [bis(trifluoroacetoxy)iodo]benzene (4.3 g, 10 mmol) in 20 ml of THF is added dropwise at −50 °C. After further 30 min at this temp. and 4 h at 0° to −10 °C the reaction mixture is worked up as described for **3b** (method a). The residue crystallizes after the addition of a small amount of acetone: 617 mg (51%) of yellow needles; m.p. 214 °C (ref.[10]: 215–219 °C).

b) To a stirred solution of the dianion **2c** (3 mmol), thionyl chloride (0.26 ml, 3.6 mmol) is added dropwise at −78 °C. After further 1.5 h at −78 °C and 1.5 h at −30 °C the reaction mixture is worked up as described for **3b** (method a). The residue is purified on silica gel with hexane/ethyl acetate (98:2): 230 mg (32%) of yellow crystals; m.p. 214 °C.

c) To a stirred solution of the dianion **2c** (3 mmol), disulfur dichloride (1.22 g, 0.72 ml, 9 mmol) is added dropwise at −78 °C. After 1 h at −78 °C and 3 h at 20 °C work-up of the reaction mixture as described for **3b** (method a), afforded: 422 mg (58%) of yellow needles after chromatography; m.p. 214 °C.

d) To a stirred solution of 2,2-diphenyl-4-(diphenylmethylene)-1,3,2-dithiastannetane (**9d**) (1.55 g, 3 mmol) in dry CH_2Cl_2 (30 ml) thionyl chloride (0.26 ml, 3.6 mmol) is added dropwise at −78 °C under N_2. After 1 h at −78 °C and 3 h at 20 °C work-up of the reaction mixture as described for **3b** (method a), furnished 170 mg (23%) of yellow needles after chromatography on silica gel with cyclohexane/ether acetate (98:2) as the second fraction; m.p. 214 °C. Byproduct is **18** (7%). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.11 (20H, m, aromat. H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3 (C-7), 140.1 (C-1′), 135.9 (C-3, -6), 129.6 (C-3′, -5′), 128.3 (C-4′), 128.2 (C-2′, -6′). – MS; *m*/*z* (%): 484 (4) [M^+], 452 (2), 242 (15), 210 (100, thioketene). – $C_{28}H_{20}S_4$ (484.7): calcd. C 69.38, H 4.16, S 26.46; found C 69.38, H 4.15, S 26.01.

4,5-Dimethyl-6-thioxopropylthio-1,2-dithiin-3-yl Propanedithioate (**6**): A solution of propanedithioic acid (**1a**, 1.06 g, 10 mmol) and triethylamine (1.39 ml, 10 mmol) in dry THF (30 ml) prepared by mixing the components slowly at −10°C is added dropwise to a stirred suspension of [bis(acetoxy)iodo]benzene (1.61 g, 5 mmol) in dry THF (30 ml) at −50°C under N_2. Stirring is continued for 1 h at this temp. and for 4 h at 0°C. The red solution is then shaken with $CHCl_3$ (30 ml)/water (30 ml) and the aqueous phase extracted with $CHCl_3$ (3 × 15 ml). The combined $CHCl_3$ layers are washed with water, dried with Na_2SO_4 and concentrated in vacuo. The obtained dark red oil is subjected to kugelrohr distillation (3 mbar, 150−200°C) and further purified by silica gel chromatography with CH_2Cl_2/hexane (65:35) as the eluant furnishing 170 mg (20%) of a dark red oil. − With (dichloro)iodobenzene: 120 mg (14%). − ^1H NMR (400 MHz, $CDCl_3$): δ = 2.88 (4H, q, CH_2), 2.18 (6H, s, 4-, 5-CH_3), 1.37 (6H, t, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 215.5 (C=S), 173.4 (C-3, -6), 141.7 (C-4, -5), 26.9 (CH_2), 15.2 (4-, 5-CH_3), 13.5 (CH_3). − MS; *m/z* (%): 178 (17) [M^+], 176 (100), 143 (28). − $C_{12}H_{16}S_6$ (352.6): calcd. C 40.87, H 4.57, S 54.56; found C 41.07, H 4.32, S 54.14.

3,5-Diisopropylidene-1,2,4-trithiolane (**7**): To a stirred solution of 2-methylpropanedithioic acid (**1b**, 0.6 g, 5 mmol) in dry THF (30 ml) triethylamine (0.69 ml, 5 mmol) is added at −10°C under N_2. After 45 min a suspension of [bis(acetoxy)iodo]benzene (1.61 g, 5 mmol) in THF (50 ml) is added in portions at −30°C. Stirring is continued for 30 min at this temp. and for 2 h at 20°C. The reaction mixture is then diluted with $CHCl_3$ (30 ml) and water (30 ml), and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are washed with water, dried with Na_2SO_4 and concentrated in vacuo. The yellow residue is then purified on silica gel with cyclohexane to provide 75 mg (15%) of yellow crystals, m.p. 112°C (ref.[13a]: 112−113°C). − ^1H NMR (400 MHz, $CDCl_3$): δ = 2.05 (6H, s, CH_3), 1.96 (6H, s, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 129.5 (C-6), 129.3 (C-3, -5), 24.41, 24.29 (2 CH_3).

4-(Diphenylmethylene)-2,2-dimethyl-1,3,2-dithiastannetane (**9b**): To a stirred solution of **10b** (1.28 g, 3 mmol) in dry THF (20 ml) LiHMDS (1 M in hexane, 3.0 ml, 3 mmol) is added dropwise at −30°C. Stirring is continued for 30 min at this temp. and for 18 h at 20°C. Then the reaction mixture is diluted with $CHCl_3$ (30 ml) and water (30 ml) and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are washed with a small amount of water, dried with Na_2SO_4 and concentrated in vacuo to give 410 mg (35%) of a colorless powder. Further purification is achieved by dropwise addition of a solution of the substance in a small amount of THF to hexane; m.p. 164−166°C. − ^1H NMR (400 MHz, [D_6]DMSO): δ = 7.24−7.16 (8H, m, aromat. H), 7.09−7.04 (2H, m, aromat. H), 0.89 [6H, s, $Sn(CH_3)_2$]. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3 (C-1′), 134.6 (C-5), 130.3 (C-4), 129.64, 127.31 (C-2′, -3′, -5′, -6′), 125.1 (C-4′), 7.5 (CH_3). − MS; *m/z* (%): 392 (2.6) [M^+], 347 (10), 210 (100). − $C_{16}H_{16}S_2Sn$ (391.1): calcd. C 49.13, H 4.12, S 16.39; found C 49.10, H 4.17, S 16.29.

4-(Diphenylmethylene)-2,2-diphenyl-1,3,2-dithiastannetane (**9d**): To a stirred solution of the dianion **2c** in dry THF − prepared from 2,2-diphenylethanedithioic acid (2.44 g, 10 mmol) and BuLi (1.6 M in hexane, 12.5 ml, 20 mmol) as described for the dianion **2b** (under **3b**, method a) − a solution of diphenyltin dichloride (3.44 g, 10 mmol) in 20 ml of THF is added dropwise at −30°C. Stirring is continued for 30 min at this temp. and for 18 h at 20°C. Then the reaction mixture is diluted with $CHCl_3$ (30 ml) and water (30 ml) and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are washed with a small amount of water, dried with Na_2SO_4 and concentrated in vacuo. The solid residue is dissolved in a small amount of $CHCl_3$ and the solution dropped into hexane (50 ml) to give 4.0 g (78%) of a beige powder; m.p. 161−164°C (dec.). − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.68−7.51 (4H, m, 2′-, 6′-H at Sn), 7.39−7.36 (6H, m, 3′-, 4′-, 5′-H at Sn), 7.21−7.15 (6H, m, 3′-, 4′-, 5′-H), 6.87 (4H, m, 2′-, 6′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7 (C-5), 142.0, 139.6 (C-1′ and C-1′ at Sn), 136.1 and 128.9 (C-2′, -3′, -5′, -6′ at Sn), 130.1 (C-4′ at Sn), 129.9, 127.6 (C-2′, -3′, -5′, -6′), 127.2 (C-4′), 122.0 (C-4). − MS; *m/z* (%): 516 (0.3) [M^+], 420 (0.3), 351 (13), 229 (15), 210 (100) [thioketene$^+$]. − FD MS; *m/z* (%): 515 (100), 515.9 (26). − $C_{26}H_{20}S_2Sn$ (515.3): calcd. C 60.60, H 3.91, S 12.44; found C 60.40, H 3.88, S 12.21.

Chlorodimethyl[(2-methyl-1-thioxopropyl)thio]tin (**10a**): To a stirred solution of 2-methylpropanedithioic acid (**1b**, 1.20 g, 10 mmol) in dry THF (20 ml), triethylamine (1.39 ml, 10 mmol) is added dropwise at −10°C and after 30 min a solution of dimethyltin dichloride (4.39 g, 20 mmol) in 30 ml of THF. Stirring is continued for 1 h at this temp. and for 4 h at room temp. Then the reaction mixture is diluted with $CHCl_3$ (30 ml) and water (30 ml) and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are washed with a small amount of water, dried with Na_2SO_4 and concentrated in vacuo. The solid residue is recrystallized from hexane to give 1.82 g (60%) of yellow needles; m.p. 75°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 3.39 (1H, sept., 2-H), 1.36 (6H, d, 2 CH_3), 1.25 [6H, s, $Sn(CH_3)_2$]. − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 265.2 (C=S), 50.7 (C-2), 24.6 (2 CH_3), 8.1 [$Sn(CH_3)_2$]. − MS; *m/z* (%): 304 (15) [M^+]. − $C_6H_{13}ClS_2Sn$ (303.4): calcd. C 23.75, H 4.32, Cl 11.68, S 21.13; found C 23.39, H 4.32, Cl 11.73, S 20.62.

Chloro[(2,2-diphenyl-1-thioxoethyl)thio]dimethyltin (**10b**): 2,2-Diphenylethanedithioic acid (**1c**, 2.44 g, 10 mmol), triethylamine (1.39 ml, 10 mmol), and dimethyltin dichloride (4.39 g, 20 mmol) are allowed to react as described for **10a**. The solid residue is dissolved in a small amount of $CHCl_3$ and the solution dropped into 20 ml of hexane to afford 2.99 g (70%) of an orange yellow powder; m.p. 85°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35−7.28 (10H, m, aromat. H), 5.80 (1H, s, 2-H), 1.23 (6H, s, 2 CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 257.1 (C=S), 140.5 (C-1′), 128.7 (C-2′, -3′, -5′, -6′), 127.7 (C-4′), 71.6 (C-2), 8.0 (CH_3). − MS; *m/z* (%): 392 (0.8) [M^+ − HCl], 210 (36), 205 (100), 203 (62), 185 (28), 165 (18), 155 (55). − $C_{16}H_{17}ClS_2Sn$ (427.6): calcd. C 44.94, H 4.01, Cl 8.29, S 14.99; found C 44.79, H 4.13, Cl 8.22, S 14.50.

Chloro[(2-methyl-1-thioxopropyl)thio]diphenyltin (**10c**): 2-Methylpropanedithioic acid (**1b**, 1.80 g, 15 mmol), triethylamine (2.08 ml, 15 mmol), and diphenyltin dichloride (5.16 g, 15 mmol) are allowed to react as described for **10a**. The oily residue crystallizes after the addition of a small amount of acetone to furnish 2.63 g (41%) of yellow crystals. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.94−7.91 (4H, m, aromat. 2′-, 6′-H), 7.51−7.43 (6H, m, aromat. 3′-, 4′-, 5′-H), 3.40 (1H, sept, 2-H), 1.35 (6H, d, 2 CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 265.3 (C=S), 140.3 (C-1′), 135.7, 129.2 (C-2′, -3′, -5′, -6′), 130.7 (C-4′), 49.6 (C-2), 24.8 (CH_3). − MS; *m/z* (%): 392 (23) [M^+ − HCl], 377 (2), 350 (3), 309 (22), 307 (20), 273 (49), 229 (34). − $C_{16}H_{17}ClS_2Sn$ (427.6): calcd. C 44.94, H 4.01, Cl 8.29, S 14.99; found C 44.64, H 3.75, Cl 8.41, S 14.87.

Dimethylbis[(2-methyl-1-thioxopropyl)thio]tin (**11a**): 2-Methylpropanedithioic acid (**1b**, 0.60 g, 5 mmol), triethylamine (0.69 ml, 5 mmol), and dimethyltin dichloride (0.55 g, 2.5 mmol) are allowed to react as described for **10a** with a stirring period of 18 h at room temp. The oily residue crystallizes after the addition of a small amount of hexane at −78 °C. At this temperature the crystals are filtered off rapidly and dissolved in $CHCl_3$. The obtained solution is concentrated in vacuo to afford 0.59 g (61%) of a yellow oil. – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.44 (2H, sept, 2 × 2-H), 1.32 (12H, d, 4 CH_3), 1.27 [6H, s, $Sn(CH_3)_2$]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 261.9 (C=S), 52.2 (C-2), 24.5 (CH_3), 9.1 [$Sn(CH_3)_2$]. – MS; *m/z* (%): 388 (0.06) [M^+], 347 (10), 345 (9), 269 (58), 267 (50), 204 (7). – $C_{10}H_{20}S_4Sn$ (387.2): calcd. C 31.02, H 5.21, S 33.12; found C 31.13, H 5.02, S 33.00.

Bis[(2,2-diphenyl-1-thioxoethyl)thio]dimethyltin (**11b**): 2,2-Diphenylethanedithioic acid (**1c**, 1.22 g, 5 mmol), triethylamine (0.69 ml, 5 mmol) and dimethyltin dichloride (0.55 g, 2.5 mmol) are allowed to react as described for **10a** with a stirring period of 18 h at room temp. The orange solid residue (1.38 g, 87%) is spectroscopically pure; it may be recrystallized from ethyl acetate to furnish 720 mg (45%) of orange yellow crystals; m.p. 149 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.23 (20H, m, aromat. H), 5.89 (2H, s, 2-H), 1.26 (6H, s, 2 CH_3). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 253.8 (C=S), 141.1 (C-1′), 128.83, 128.41 (C-2′, -3′, -5′, -6′), 127.3 (C-4′), 73.3 (C-2), 9.2 (CH_3). – MS; *m/z* (%): 529 (2), 527 (2.5), 347 (14), 242 (11), 210 (100, thioketene). – $C_{30}H_{28}S_4Sn$ (635.5): calcd. C 56.70, H 4.44, S 20.18; found C 56.47, H 4.49, S 19.82.

4,6-Diisopropylidene-2,2-dimethyl-1,3,5,2-trithiastanninane (**13**): a) To a stirred solution of **10a** (0.91 g, 3 mmol) in dry diethyl ether (20 ml), triethylamine (0.46 ml, 3.3 mmol) is added dropwise at −30 °C. Stirring is continued for 1 h at this temp. and for 3 h at 20 °C. The precipitate (triethylamine hydrochloride) is filtered off and the filtrate concentrated in vacuo. The residue solidifies by the addition of a small amount of hexane to give a colorless powder containing **13**, about 20% of **14**, and a small amount of **7** (according to NMR analysis). By repeated precipitation with hexane **14** is nearly eliminated with the first crystalline fractions. **13** was not obtained in analytically pure form. 170 mg (32%) of colorless powder; m.p. 85–94 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.08, 2.04 (12H, s, 4 CH_3), 0.82 [6H, s, $Sn(CH_3)_2$]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.5 (C-7), 118.7 (C-4, -6), 24.37, 23.48 (2 CH_3), 1.1 [$Sn(CH_3)_2$]. – MS, *m/z* (%): 354 (28) [M^+], 268 (80), 266 (59), 253 (32), 251 (24), 238 (7), 204 (6). FD-MS: 353.9 (47%), 353.0 (100%). – $C_{10}H_{18}S_3Sn$: calcd. 353.9592; found 353.9582.

b) To a stirred solution of the dianion **2b** (5 mmol) in THF – prepared as described for **3b**, method a) – a solution of dimethyltin dichloride (1.1 g, 5 mmol) in 30 ml of THF is added dropwise at −30 °C. Then method a is applied: 70 mg (8%) of **13** as a colorless powder.

2,4,6-Hexamethyl-1,3,5,2,4,6-trithiatristanninane (**14**): Compound **14** is obtained as a byproduct in the preparation of **13**. **14** separates first after the addition of hexane as described in the purification procedure of **13**. It is recrystallized from hexane to furnish 50 mg colorless crystals; m.p. 150–152 °C [ref.[15]: 149–151 °C]. – ^1H NMR ($CDCl_3$): δ = 0.87 (s, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 4.75 (s, CH_3). – $C_6H_{18}S_3Sn_3$ (542.5): calcd. C 13.28, H 3.34, S 17.73; found C 13.26, H 3.32, S 17.46.

2,4-Bis(diphenylmethylene)-1,3-dithietane (**15**): a) A solution of **9d** (0.26 g, 0.5 mmol) in $CHCl_3$ (10 ml) is allowed to stand at 20 °C for 40 d. The precipitate is filtered off and recrystallized from $CHCl_3$ to furnish 30 mg (28%) of yellow needles; m.p. 267 °C (ref.[10]: 263 °C).

b) A solution of THF of the dianion **2c** – obtained from 2,2-diphenylethanedithioic acid (**1c**, 0.98 g, 4 mmol) and BuLi (1.6 M in hexane, 5 ml, 8 mmol) as described for the dianion **2b** (under **3b**, method a) – is treated at −78 °C with trimethylsilyl chloride (0.96 g, 1.11 ml, 8 mmol). Stirring is continued for 15 min at this temp. and for 2 h at 20 °C. Then the reaction mixture is concentrated in vacuo, the residue is heated in a kugelrohr apparatus at 0.1 Torr to eliminate volatile impurities and finally recrystallized from $CHCl_3$ to provide 110 mg (13%) of yellow needles; m.p. 267 °C. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.30 (8H, m, aromat. H), 7.25–7.20 (12H, m, aromat. H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1 (C-1′), 130.3 (C-5), 128.7 (C-2′, -3′, -5′, -6′), 127.3 (C-4′), 117.8 (C-4). – MS; *m/z* (%): 420 (72) [M^+], 210 (100, thioketene), 178 (12), 165 (41). – $C_{28}H_{20}S_2$ (420.6): calcd. C 79.96, H 4.79, S 15.25; found C 79.50, H 4.56, S 15.23.

3,5-Bis(diphenylmethylene)-1,2,4-trithiolane (**16**): a) To a solution of the dianion **2c** in THF – obtained from 2,2-diphenylethanedithioic acid (**1c**, 0.73 g, 3 mmol) and BuLi (1.6 M in hexane, 3.75 ml, 6 mmol) as described for the dianion **2b** (under **3b**, method a) – a solution of dimethyltin dichloride (0.66 g, 3 mmol) in 5 ml of THF is added dropwise with stirring at −50 °C. Stirring is continued for 4 h at room temp. Work-up of the reaction mixture as described for **3b** affords a residue which is purified by chromatography on silica gel with hexane/ethyl acetate (95:5) to give 140 mg (21%) of yellow crystals; m.p. 198 °C (from acetone), [ref.[20]: 193–194 °C]. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.21 (20H, m, aromat. H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.98, 141.25 (2 × C-1′), 136.48, 135.74 (C-3, -5, 2 × C-6), 129.43, 129.38, 128.31, 128.22 (2 × C-3′, -5′, 2 × C-2′, -6′), 128.03, 127.91 (2 × C-4′). – MS; *m/z* (%): 452 (18) [M^+], 420 (6), 242 (5), 210 (100). – $C_{28}H_{20}S_3$ (452.6): calcd. C 74.29, H 4.45, S 21.25; found C 74.02, H 4.16, S 21.30.

b) To a solution of **11b** (1.27 g, 2 mmol) in dry THF (30 ml), LiHMDS (1 M in hexane, 4.0 ml, 4 mmol) is added dropwise with stirring at −20 °C. Stirring is continued for 30 min at this temp. and for 2 h at 20 °C. Then the reaction mixture is cooled to −10 °C and treated slowly with iodine (0.25 g, 1 mmol) in 20 ml of THF. After 3 h at room temp. $CHCl_3$ (30 ml) and water (30 ml) are added and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are washed with an aqueous solution of KI, dried with Na_2SO_4 and concentrated in vacuo. The solid residue is recrystallized from acetone to afford 500 mg (55%) of yellow plates; m.p. 198 °C.

c) To a solution of the dianion **2c** (5 mmol) in dry THF – see method a and **3b** (method a) – elemental sulfur (0.51 g, 2 mmol) is added in several portions with stirring at −40 °C. Stirring is continued for 1 h at this temp. and for 4 h at 20 °C. Then $CHCl_3$ (30 ml) and water (30 ml) are added and the aqueous phase is extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers are dried with Na_2SO_4 and concentrated in vacuo. The residue is purified by chromatography on silica gel to give 430 mg (38%) of **6** (yellow crystals, m.p. 198 °C) and 56 mg (5%) of **17** [orange red crystals; m.p. 162–164 °C (from acetone)].

2-(Diphenylmethylene)-4,4-diphenyl-1,3-dithiolane-5-thione (**17**): Compound **17** is formed as a byproduct of **16**. Orange red crystals. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.10 (20H, m, aromat. H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 236.7 (C=S), 140.26 [2 × C-1 (4-phenyl)], 140.23, 140.19 [2 × C-1 (6-phenyl)], 135.0 (C-6), 129.48, 127.98 [C-2, -3, -5, -6 (4-phenyl)], 127.98 [2 × C-4 (4-phenyl)], 129.32, 128.96, 128.47, 128.37 [2 × C-2, -3, -5, -6 (6-phenyl)], 128.27 [2 × C-4 (6-phenyl)], 127.77 (C-2), 84.3 (C-4). – MS; *m/z* (%): 452 (26) [M^+], 376 (11), 299 (15), 210 (100). – FD-MS: 451.9 (100%). – $C_{28}H_{20}S_3$ (452.6): calcd. C 74.29, H 4.45, S 21.25; found C 74.14, H 4.34, S 21.10.

7-Diphenylmethylene-1,2,3,4,5,6-hexathiepane (**18**): a) To a solution of disulfur dichloride (0.29 ml, 3.6 mmol) in dry CH_2Cl_2 (20 ml), a solution of **9d** (1.55 g, 3 mmol) in CH_2Cl_2 (30 ml) is added dropwise at −78°C with stirring. Stirring is continued for 1 h at this temp., for 1.5 h at −50°C and for 3 h at −5°C. Then $CHCl_3$ (20 ml) and water (20 ml) are added and the aqueous phase is extracted with $CHCl_3$ (3 × 10 ml). The combined organic layers are washed with a small amount of water, dried with Na_2SO_4 and concentrated in vacuo. The solid residue is purified on silica gel with hexane/ethyl acetate (98:2) to give as first fraction 180 mg (16%) of light yellow crystals, m.p. 160−166°C. The second fraction contains **19**, the third fraction **20**. − ^1H NMR (400 MHz, $[D_8]THF$): δ = 7.34−7.21 (6H, m, aromat. H), 7.19−7.18 (4H, m, aromat. H). − ^{13}C NMR (100 MHz, $[D_8]THF$): δ = 149.5 (C-8), 143.8 (C-7), 142.9 (C-1′), 130.49, 128.97 (C-2′, -3′, -5′, -6′), 129.34 (C-4′). − MS; *m/z* (%): 370 (2.5) $[M^+]$, 306 (13), 274 (4), 242 (58), 210 (100, thioketene), 178 (11), 165 (75), 54 (28). − FD-MS: 370.0 (100). − $C_{14}H_{10}S_6$ (370.6): calcd. C 45.37, H 2.72, S 51.91; found C 45.38, H 2.88, S 51.08.

b) With **9d** (3 mmol) and sulfur dichloride (0.18 ml, 3.6 mmol) according to method a): first fraction: 135 mg (12%) of light yellow crystals; m.p. 160−166°C. The second fraction contains **19**, the third fraction **20**.

c) Byproduct in the preparation of **3c** (method d): 75 mg (7%) of light yellow crystals; m.p. 160−166°C.

4,8-Bis(diphenylmethylene)-1,2,3,5,6,7-hexathiocane (**19**): a) Byproduct in the preparation of **18** with disulfur dichloride (method a) as second fraction: 30 mg (4%) of light yellow crystals; m.p. 163−168°C. − b) Byproduct in the preparation of **18** with sulfur dichloride (method b) as second fraction: 83 mg (10%) of light yellow crystals; m.p. 163−168°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.31−7.23 (20H, m, aromat. H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2 (C-9), 141.5 (C-1′), 136.6 (C-8), 129.88, 128.52 (C-2′, -3′, -5′, -6′), 128.63 (C-4′). − MS; *m/z* (%): 306 (11), 274 (3), 242 (61), 210 (100), 178 (11), 165 (70), 64 (18). FD-MS: 548.0 (100%). − $C_{28}H_{20}S_6$ (548.8): calcd. C 61.27, H 3.67, S 35.05; found C 60.79, H 3.52, S 34.73.

4,7-Bis(diphenylmethylene)-1,2,3,5,6-pentathiepane (**20**): a) Byproduct in the preparation of **18** with disulfur dichloride (method a) as third fraction: 30 mg (4%) of light yellow crystals; m.p. 163−172°C (from acetone). − b) Byproduct in the preparation of **18** with sulfur dichloride (method b) as third fraction: 45 mg (6%) of light yellow crystals; m.p. 163−172°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33−7.25 (12H, m, aromat. 3′-, 4′-, 5′-H), 7.19−7.15 (8H, m, aromat. 2′-, 6′-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0 (C-8), 135.0 (C-7), 141.94, 140.96 (2 × C-1′), 130.09, 129.84, 128.12, 127.95 (C-2′, -3′, -5′, -6′), 128.67, 128.29 (2 × C-4′). − MS; *m/z* (%): 306 (7) $[M^+]$, 274 (3), 242 (50), 210 (100), 165 (50), 64 (27). − FD-MS: 516.0 (100%). − $C_{28}H_{20}S_5$ (516.8): calcd. C 65.07, H 3.90, S 31.02; found C 64.70, H 3.88, S 30.57.

4,7-Diisopropylidene-1,2,3,5,6-pentathiepane (**21**): Byproduct in the preparation of **3b** (method b): third fraction, 100 mg (8%) of light yellow crystals; m.p. 115−123°C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 2.18 (6H, s, CH_3), 2.09 (6H, s, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5 (C-8), 130.3 (C-7), 25.13, 24.69 (2 × CH_3). − MS; *m/z* (%): 268 (19) $[M^+]$, 236 (10), 204 (5), 182 (22), 150 (24), 86 (100, thioketene), 71 (26), 41 (17). − $C_8H_{12}S_5$ (268.5): calcd. C 35.78, H 4.51, S 59.71; found C 35.99, H 4.22, S 59.26.

7-Isopropylidene-1,2,3,4,5,6-hexathiepane (**22**): Byproduct in the preparation of **3b** (method b): first fraction, 10 mg (0.5%) of yellow crystals, m.p. 39−45°C. Due to lack of substance no complete analytical characterization was possible. − ^1H NMR (400 MHz, $CDCl_3$): δ = 2.15 (6H, s, CH_3). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.4 (C-8), 137.5 (C-7), 26.1 (CH_3). − MS; *m/z* (%): 246 (26) $[M^+]$, 182 (63), 86 (100), 71 (36), 64 (27), 45 (13).

☆ Dedicated to Prof. Dr. *Kurt Dehnicke* on the occasion of his 65th birthday.

[1] K. Hartke, N. Rettberg, D. Dutta, H.-D. Gerber, *Liebigs Ann. Chem.* **1993**, 1081−1089, and references to previous literature given herein.

[2] U. Wagner, Ph. D. Thesis, University of Marburg, **1995**.

[3] Review of dithiocarboxylic acids, their salts and esters: [3a] R. Mayer, S. Scheithauer, *Methoden Org. Chem. (Houben-Weyl), 4. Ed.* **1985**, *Vol. E5*, 891−930, p. 921. − [3b] S. Scheithauer, R. Mayer in *Topics in Sulfur Chemistry*, Ed. A. Senning, Vol. 4, p. 282, Thieme, Stuttgart **1979**.

[4] R. Gompper, W. Töpfl, *Chem. Ber.* **1962**, *95*, 2861−2870.

[5] P. Yates, Th. R. Lynch, *Can. J. Chem.* **1971**, *49*, 1477−1488.

[6] A. J. Kirby, *Tetrahedron* **1966**, *22*, 3001−3005.

[7] Review: R. M. Moriarty, R. K. Vaid, *Synthesis* **1990**, 431−447.

[8] M. S. Raasch, *J. Org. Chem.* **1970**, *35*, 3470−3483.

[9] H. Bühl, U. Timm, H. Meier, *Chem. Ber.* **1979**, *112*, 3728−3736.

[10] A. Schönberg, E. Frese, K.-H. Brosowski, *Chem. Ber.* **1962**, *95*, 3077−3083.

[11] W. Schroth, H. Jordan, R. Spitzner, *Tetrahedron Lett.* **1995**, *36*, 1421−1425. Leading references are summarized here.

[12] E. Schaumann, F.-F. Grabley, *Liebigs Ann. Chem.* **1979**, 1702−1714.

[13] [13a] U. Kunze, R. Merkel, W. Winter, *Angew. Chem.* **1982**, *94*, 300−301 and 301−302 [*Int. Ed. Engl.* **1982**, *21*, 290 and 291. − [13b] U. Kunze, R. Merkel, W. Winter, *Chem. Ber.* **1982**, *115*, 3653−3662.

[14] Ch. Bonnans-Plaisance, J.-C. Gressier, G. Levesque, A. Mahjoub, *Bull. Soc. Chim. Fr.* **1985**, 891−899.

[15] Review: G. Bähr, S. Pawlenko, *Methoden Org. Chem. (Houben-Weyl), 4. Ed.* **1978**, *Vol. 13/6*, 335−353.

[16] [16a] S. Kato, M. Mizuta, *J. Organomet. Chem.* **1973**, *55*, 121−132. − [16b] S. Kato, T. Kato, T. Yamauchi, Y. Shibahashi, E. Kakuda, M. Mizuta, Y. Ishii, *J. Organomet. Chem.* **1974**, *76*, 215−224. − [16c] S. Kato, A. Hori, H. Shiotani, M. Mizuta, *J. Organomet. Chem.* **1974**, *82*, 223−230. − [16d] S. Kato, Y. Ono, K. Miyagawa, T. Murai, M. Ishida, *Tetrahedron Lett.* **1986**, *27*, 4595−4598.

[17] [17a] F. Fehér, M. Langer, *Tetrahedron Lett.* **1971**, 2125−2126. − [17b] I. W. J. Still, G. W. Kutney, *Tetrahedron Lett.* **1981**, *22*, 1939−1940. − [17c] U. Anthoni, C. Christophersen, N. Jacobsen, A. Svendsen, *Tetrahedron* **1982**, *38*, 2425−2427. − [17d] R. Sato, S. Saito, H. Chiba, T. Goto, M. Saito, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1647−1651. − [17e] H. Bock, B. L. Chenards, P. Rittmeyer, U. Stein, *Z. Naturforsch.* **1988**, *43b*, 117−124. − [17f] N. Tokitoh, H. Hayakawa, M. Goto, W. Ando, *Tetrahedron Lett.* **1988**, *29*, 1935−1939. − [17g] W. Lutz, T. Pilling, G. Rihs, H. R. Waespe, T. Winkler, *Tetrahedron Lett.* **1990**, *31*, 5457−5458. − [17h] N. Tokitoh, Y. Okano, W. Ando, *Tetrahedron Lett.* **1990**, *31*, 5323−5326. − [17i] R. Steudel, M. Kustos, *Phosphorus, Sulfur, Silicon* **1991**, *62*, 127−137. − [17j] M. Kustos, J. Pickardt, J. Albertsen, R. Steudel, *Z. Naturforsch., Teil B* **1993**, *48*, 928−934. − [17k] N. Takeda, N. Tokitoh, T. Imakubo, M. Goto, R. Okazaki, *Bull. Chem. Soc. Jpn.* **1995**, 2557−2564.

[18] [18a] S. J. Wratten, D. J. Faulkner, *J. Org. Chem.* **1976**, *41*, 2465−2467. − [18b] B. S. Davidson, T. F. Molinski, L. R. Barrows, C. M. Ireland, *J. Am. Chem. Soc.* **1991**, *113*, 4709−4710. − [18c] P. W. Ford, M. R. Narbut, J. Belli, B. S. Davidson, *J. Org. Chem.* **1994**, *59*, 5955−5960. − [18d] F. D. Toste, I. W. J. Still, *J. Am. Chem. Soc.* **1995**, *117*, 7261−7262.

[19] A. Schönberg, A. Stephenson, H. Kaltschmitt, E. Petersen, H. Schulten, *Ber. Dtsch. Chem. Ges.* **1933**, *66*, 237−244.

[20] H. J. Kyi, K. Praefcke, *Tetrahedron Lett.* **1975**, 555−558.

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