(1'RS, 2SR, 3RS)-4'-Bromo-1'-hydroxy-3-phenylspiro[tetrahydrofuran-2, 2'-(1'H-naphthalen)]-5-one (**16**) and its *(1'RS,2RS,3SR) stereoisomer* **17**. Compound **14** (1.8 g) reduced as **3** with $NaBH_4$ gave the isomers **16** and **17** in a 3:2 ratio (TLC.). Product **17** crystallized from ether/petroleum ether in the cold giving 220 mg pure product, m.p. 167–168°. – NMR. ($CDCl_3/D_2O$): 4.9 (*s*, H–C(1')), 4.2 (*t*, *J* = 4, H–C(3)), 2.95 (*d*, *J* = 4, 2 H–C(4)). – $C_{19}H_{15}BrO_3$: C, H, Br.

The mother liquor was evaporated to dryness and toluene was added from which 250 mg of **16** were isolated, m.p. 182–185°. – NMR. ($CDCl_3/D_2O$): 5.4 (*s*, H–C(1')), 4.0 (*d* × *d*, *J* = 6, 10, H–C(3)), 3.3 (*d* × *d*, *J* = 10, 16, H_A–C(4)), 2.7 (*d* × *d*, *J* = 6, 16, H_B–C(4)). – $C_{19}H_{15}BrO_3$: C, H, Br.

(1'RS,2SR,3RS)-1'-Hydroxy-3-phenylspiro[tetrahydrofuran-2, 2'-(1'H-naphthalen)]-5-one (**18**) and its *(1'RS,2RS,3SR) stereoisomer* **19**. As above from 100 mg of **15** about 100 mg of an oil were obtained containing a 3:2 ratio of **18** and **19** respectively (TLC.). Both products were separated on *Macherey-Nagel* precoated TLC. plates Sil G-100 UV_{254} eluted with heptane/$CHCl_3$/ethanol, 65:35:10. Product **18**, Rf 0.43, 50 mg, crystallized from ether, m.p. 165–169°. Product **19**, Rf 0.37, 38 mg, crystallized from ether/pet. ether, m.p. 142–144°.

(1'RS, 2SR, 3RS)-3, 3', 1'-Hydroxy-3-phenylspiro[tetrahydrofuran-2, 2'-(1', 2', 3', 4'-tetrahydronaphthalen)]-5-one (**20**). – 1) *From* **16**. The bromo-compound **16** (150 mg) hydrogenated as **5** gave **20** (35 mg), m.p. 150–151°. – NMR. ($CDCl_3/D_2O$): 4.8 (*s*, H–C(1')). – $C_{19}H_{18}O_3$: C, H.

2) *From* **18**. The olefinic compound **18** (50 mg) hydrogenated as **5** gave **20** (25 mg), m.p. 149–150°. – NMR.: superimposable with that of **20** obtained from **16**. – $C_{19}H_{18}O_3$: C, H.

6-Bromo-4-phenylbenzo[h]*chroman-2-one* (**21**). As for the preparation of **1** from **5**, compound **21** was obtained in quantitative yield from **16**, m.p. 158–160°. – NMR.: 7.3 (*s*, H–C(5)), 4.4 (*t*, *J* = 6, H–C(4)), 3.1 (*d*, *J* = 6, H–C(3)). – $C_{19}H_{13}BrO_2$: C, H, Br.

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140. A Short Synthesis of 3,5-Dimethyl-1,2,4-trithiolane

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(11.IV.78)

Summary

A short synthesis of 3,5-dimethyl-1,2,4-trithiolane (**1**), a well-known constituent of processed meat, is described.

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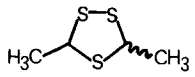
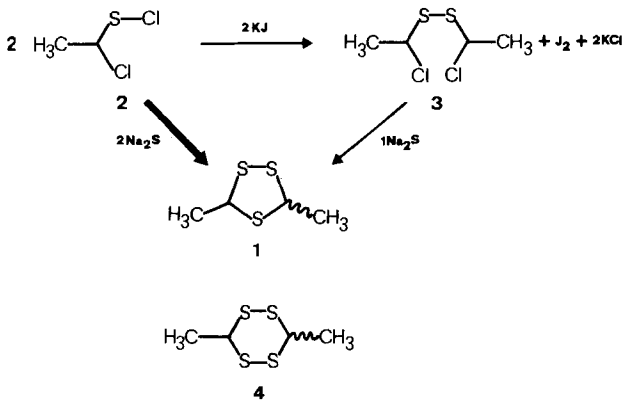
During their analytical studies of the volatiles of roasted pork meat, *Hrivnac et al.* [1] detected *cis*- and *trans*-3,5-dimethyl-1,2,4-trithiolane (**1**). This finding is in line with the observations of *Chang et al.* [2] and of *Brinkman et al.* [3] who isolated the same compounds from beef broth as well as from boiled beef.



1

From a synthetic viewpoint, the 1,2,4-trithiolanes are not extensively investigated, despite their interesting properties as flavouring agents. *Asinger* [4] described the synthesis of various 3,5-dialkyl substituted derivatives, although in low yields (*e.g.* 5% for the mixture of compounds **1**), by reaction of the corresponding aldehydes with an amine in the presence of hydrogen sulfide and sulfur. *Tjan et al.* [5] have reported a very interesting approach to such systems, which is outlined within the *Scheme* for 3,5-dimethyl-1,2,4-trithiolane (**1**). They reacted the α-chloroethyl sulfenylchloride (**2**), easily obtained by chlorination of diethyl-disulfide [6], in a reductive step with potassium iodide to the dichloro disulfide **3** [7] (yield: 79%). Compound **3**, in turn, was subsequently cyclized with one molar equivalent of sodium sulfide to give **1** in an overall yield of 21%. We have found that the mentioned two-step synthesis of the 1,2,4-trithiolane **1** can be shortened. When the α-chloroethyl sulfenylchloride (**2**) was treated with one molar equivalent of sodium sulfide, both, the reductive dimerization and the cyclization were effected in one step, giving the 1,2,4-trithiolane **1** in 32% yield. During this transformation elemental sulfur was formed. The remainder of the reaction mixture was mainly consisting of non-volatile parts. But, in addition, we could isolate 3,6-dimethyl-1,2,4,5-tetrathiacyclohexane (**4**) in approximately 8% yield. Compound **4** is known to occur in processed ham [8] as well.

Scheme



The authors are indebted to Dr. *P. Schudel* for stimulating discussions and to Mr. *Y.-St. Kellenberger* for his skillful experimental help.

Experimental Part

General remarks. ^{1}H-NMR. spectra were recorded on a *Varian* XL-100A instrument (100 MHz), using $CDCl_3$ as solvent and TMS as internal standard (ppm-values relative to TMS = 0 ppm), abbreviations: *d* = doublet, *qa* = quartet, *J* = spin-spin coupling constant (Hz). IR. spectra were measured on a *Perkin-Elmer* 257 spectrometer; characteristic maxima are given in cm^{-1}. Mass spectra were recorded on a *Varian* CH-5 spectrometer, using an inlet temperature of 150° and an ionisation energy of 70 eV; the intensity of the molecular ion and of the eight most intense fragment ions are given in % of the base pik. Gas liquid chromatography (GLC.) was performed on a *Carlo Erba* Fractovap GI instrument, using OV 101, 2% on AW-DMCS, 80–100 mesh (3 mm × 3 m).

Starting materials. Diethyl disulfide was chlorinated to give α-chloroethyl-sulfenylchloride (**2**), as described in [5].

3,5-Dimethyl-1,2,4-trithiolane (**1**). α-Chloroethyl-sulfenylchloride (**2**) (78.6 g, 0.6 mol) was dropwise added, within 1 h to a well-stirred solution of $Na_2S \cdot 9\,H_2O$ (144 g, 0.6 mol) in 1 l of dimethylformamide. A temperature-rise to 40° took place during addition. Stirring at ambient temperature was continued for 4 h. Formation of sulfur was observed. The reaction mixture was diluted with 1.5 l of a saturated NaCl-solution and then extracted with four 1 l-portions of hexane. The organic phases were twice washed with small portions of a saturated NaCl-solution, combined, filtered to remove residual elemental sulfur and dried over dehydrated Na_2SO_4. The solvent was evaporated at 40°/13 Torr. The crude product was subjected to a fractional distillation through a *Widmer*-column, whereby 14.8 g (32.4%) of pure (GC.) 3,5-dimethyl-1,2,4-trithiolane (**1**) (mixture of both isomers) was obtained (b.p.: 77–78°/13 Torr; $n_D^{20} = 1.5971$). – IR. (liq.): 2990, 2950, 2880, 1445, 1370, 1260, 1185, 1050, 1040, 975, 710, 675. – ^{1}H-NMR.: 5.05 and 4.90 (2*qa*, *J* = 7, 2 H, H–C(3) and H–C(5)); 1.77 and 1.65 (2*s*, *J* = 7, 6 H, 2 CH_3). – MS.: 152 (*M*, 100), 92 (66), 59 (63), 88 (62), 64 (46), 60 (36), 55 (25), 45 (23).

The last fractions of the above distillation contained 3,6-dimethyl-1,2,4,5-tetrathiacyclohexane (**4**) in enriched form (approximately 8% of total crude product). A small part of this enriched material was subjected to a preparative GC.-separation on a OV-101-column, whereby a pure sample of **4** was obtained. – IR. (liq.): 2970, 2920, 2860, 1440, 1370, 1195, 1165, 1070, 1055, 1030, 965, 705, 690. – ^{1}H-NMR.: 4.62 (*qa*, *J* = 7, 2 H, H–C(3) and H–C(6)); 1.55 (*d*, *J* = 7, 6 H, 2 CH_3). – MS.: 184 (*M*, 34), 59 (100), 60 (77), 45 (35), 124 (32), 64 (24), 92 (14), 119 (12), 152 (12).

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