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Synthesis of Sulfur-Rich Organic Polysulfanes Utilizing Titanocene Pentasulfide as a Sulfur-Transfer Reagent

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Titanocene pentasulfide, Cp_2TiS_5 (**1**) reacts with Ph_3CCl (**4**), $C_2H_4(SCl)_2$ (**6**), and $CH_3C_6H_3(SCl)_2$ (**9**) to give the corresponding polysulfanes $(Ph_3C)_2S_5$ (**5**), $C_2H_4S_7$ (**7**), and $CH_3C_6H_3S_7$ (**8**) which have been characterized by NMR, mass, and Raman spectroscopy. By interconversion reactions the mentioned polysulfanes yield homologous molecules with up to 11 sulfur atoms which have been separated by reversed-phase HPLC. Linear relationships between the capacity factor and the number of sulfur atoms in the molecule have been derived for each series, and retention indices have been calculated.

Organic polysulfanes R_2S_n ($n > 2$) may be synthesized by a variety of methods[2)] either starting from thiols, sulfenyl chlorides, elemental sulfur, sulfanes (H_2S_n), chlorosulfanes (S_nCl_2), ionic polysulfides (e. g. Na_2S_n), or other reagents. In most cases mixtures of polysulfanes of different chain length are obtained and have to be separated by careful crystallization or chromatography due to the thermal and thermodynamic instability of longer chain polysulfanes which tend to either equilibrate with species of other chain lengths or split off S_8, S_7, or S_6[3)] [eq. (1), (2)].

$$2\,R_2S_n \longrightarrow R_2S_{n+x} + R_2S_{n-x} \qquad (1)$$

$$R_2S_n \longrightarrow R_2S_{n-8} + S_8 \qquad (2)$$

Titanocene polysulfides react with various nonmetal halides as sulfur-transfer reagents[3-6)], the most famous reaction of this type being the synthesis of cycloheptasulfur, S_7, from Cp_2TiS_5 (**1**) and S_2Cl_2[5)] ($Cp = \eta^5\text{-}C_5H_5$). To our knowledge, the only application of this type of reaction to organic polysulfides is the preparation of $(C_2O_2)_2S_{10}$ (**2**) from oxalyl chloride[6)] [eq. (3)].

$$\underset{\mathbf{1}}{2\,Cp_2TiS_5} + 2\,(COCl)_2 \longrightarrow \underset{\mathbf{2}}{(C_2O_2)_2S_{10}} + \underset{\mathbf{3}}{2\,Cp_2TiCl_2} \qquad (3)$$

2 has been characterized by X-ray crystallography and forms a fourteen-membered ring with two S_5 units bridging the two C_2O_2 groups. On the other hand, Shaver et al.[7)] showed that $Cp_2Ti(SR)_2$ reacts even with benzyl bromide in boiling toluene to give the corresponding mixed monosulfide (R = alkyl or aryl) [eq. (4)].

$$Cp_2Ti(SR)_2 + 2\,PhCH_2Br \longrightarrow Cp_2TiBr_2 + 2\,PhCH_2SR \qquad (4)$$

This shows that either organic halides or sulfur halides may be treated with titanocene polysulfides. In this paper we report on the preparation of aliphatic and aromatic linear and cyclic organic polysulfanes ($R-S_n-R$) by reaction of either sulfenyl chlorides or chlorotriphenylmethane with titanocene pentasulfide. Compounds with up to seven sulfur atoms in a chain or ring have been obtained in this way in good yields.

Bis(triphenylmethyl)pentasulfane (5)

It has been found that chlorotriphenylmethane (**4**) reacts with titanocene pentasulfide (**1**) at 20°C to give the pentasulfane (**5**) in high yield [eq. (5)].

$$\underset{\mathbf{4}}{2\,Ph_3CCl} + 1 \xrightarrow{CS_2} \underset{\mathbf{5}}{(Ph_3C)_2S_5} + 3 \qquad (5)$$

3 and **5** are separated chromatographically, and **5** is isolated in 83% yield. This method is much more convenient than the previously published systhesis of **5** form the thermally labile Ph_3CSSH by reaction with SCl_2[8)]; **5** forms colorless crystals of m.p. 156°C (dec., heating rate 5°C/min) which can be heated to 100°C for 15 min without decomposition. This method is used to remove traces of solvents which the crystals of **5**, obtained from various solvents, always contain, and which are probably responsible for the lower melting point given in ref.[8)].

Heating of the crystals obtained from a $CHCl_3$/EtOH solution in an oil-pump vacuum to 96°C for 15 min yields a substance with correct analytical data. Both the reaction (5) and the thermal decomposition have been monitored by reversed-phase HPLC by using an octadecylsilane stationary phase and methanol as an eluent. As reference materials the analogous (triphenylmethyl)tri- and -tetrasulfanes have been prepared from Ph_3CSH and SCl_2 or S_2Cl_2 and characterized by C,H analysis and molecular spectra (IR, Raman, ^1H and ^{13}C NMR; see Experimental). As has been observed in many other cases the retention times t_r of $(Ph_3C)_2S_n$ increase with the number of sulfur atoms in the molecule. Since the retention times depend on the flow, the column

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length, and other parameters of the chromatographic system we have introduced the retention indices *RS* which relate the t_r value of a substance to the retention behavior of sulfur rings S_n in the same HPLC apparatus[9]. *RS* values are independent of the eluent flow and the geometry of the apparatus but do depend on the eluent composition. *RS* values measured in different laboratories can therefore directly be compared by using the same type of eluent and the same stationary phase. The *RS* values of $(Ph_3C)_2S_n$ molecules are given in Table 1.

Table 1. Retention indices *RS* of the molecules of three homologous series of polysulfanes (n = number of S atoms; eluent: methanol; stationary phase: octadecylsilane; temp. 21 °C; reference substances: S_6, S_8, S_9, S_{10})

n	$(Ph_3C)_2S_n$	$C_2H_4S_n$	$CH_3C_6H_3S_n$
2	677	–	–
4	789	–	–
5	867	420	691
6	945	–	749
7	1004	622	813
8	1090	719	–
9	1167	794	973
10	1232	920	1069
11	1293	1016	1129

Heating of solid **5** to 110 °C for 15 min followed by cooling to 20 °C, dissolution in CH_2Cl_2, and HPLC analysis shows that a mixture of $(Ph_3C)_2S_n$ molecules with n ranging from 2 to 11 has formed, the *RS* data of which are listed in Table 1. The evidence that the molecules detected by HPLC are members of a homologous series follows from the fact that the capacity factor k' ($k' = t_r - t_o/t_o$; t_o = dead time) is a linear function of the number of sulfur atoms when a semilogarithmic plot is applied. For the present molecules the relationship

$$\ln k' = 0.2464 \cdot n + 0.0400$$

was obtained (correlation coefficient $r = 0.999$; eluent: CH_3OH; $n = 3-9$; $t_o = 1.390$ min). This function allows the estimation of the retention time of unknown members of the series by extrapolation.

1,2,3,4,5,6,7-Heptathionane (7)

The 1,2-bis(sulfenyl chloride) **6** of ethane[10] reacts with **1** at 20 °C in CH_2Cl_2 within 1 h quantitatively according to eq. (6).

$$\underset{\mathbf{6}}{C_2H_4(SCl)_2} + \mathbf{1} \longrightarrow \underset{\mathbf{7}}{C_2H_4S_7} + \mathbf{3} \qquad (6)$$

HPLC analysis of the reaction mixture reveals the presence of homologous molecules $C_2H_4S_n$ (n = 5, 8, 9, 10, 11) in trace amounts obviously as a result of a secondary interconversion reaction as illustrated in eq. (7).

$$2\,C_2H_4S_n \longrightarrow C_2H_4S_{n-x} + C_2H_4S_{n+x} \qquad (7)$$

Pure **7** was isolated by column chromatography in 31% yield.

The retention data of all six observed $C_2H_4S_n$ molecules can be summarized in the linear equation

$$\ln k' = 0.3484 \cdot n - 2.0736$$

(correlation coefficient $r = 0.999$; eluent: CH_3OH; t_o = 1.390 min) which can serve to identify novel members of this series by HPLC. The retention indices *RS* are given in Table **1**.

The novel compound **7** forms yellow, odorless crystals which reversibly melt at 63 °C and which have been identified by elemental analysis, ^{1}H-NMR spectra (singlet at δ = 3.519; $CDCl_3$), and EI mass spectrometry (molecular ion peak at m/z = 252). The sulfur content of **7** is as high as 89%! A DSC measurement (differential scanning calorimetry) of **7** does not show any exo- or endothermic processes up to 110 °C besides the melting at 63 °C (heating rate 5 °C/min). However, above 115 °C an endothermic process starts which does not result in a definite peak in the DSC curve but rather in a change of the slope of the base line. Samples of **7** heated to above 115 °C are insoluble. Therefore, the endothermic process is interpreted as a polymerization of the cyclic $C_2H_4S_7$ molecules to give a linear polymer.

The UV spectrum of **7** recorded in CH_2Cl_2 is characterized by a peak at λ = 290 nm; the Raman spectrum of solid **7** shows the S–S stretching vibrations at $\tilde{\nu}$ = 419, 437, 447, 468, 490, and 509 cm^{-1}. The strongest Raman line is observed at 196 cm^{-1} (S–S–S bending mode).

9-Methyl-1,2,3,4,5,6,7-benzoheptathionine (8)

By analogy with the synthesis of **7** the title compound has been prepared in 61% yield by reaction of the bis(sulfenyl chloride) **9**[11] with **1** in CCl_4 at 20 °C according to eq. (8).

$$\underset{\mathbf{9}}{CH_3C_6H_3(SCl)_2} + \mathbf{1} \longrightarrow \underset{\mathbf{8}}{CH_3C_6H_3S_7} + \mathbf{3} \qquad (8)$$

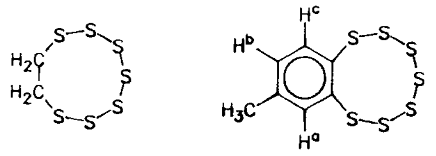
Reaction (8) proceeds almost instantaneously. HPLC analysis of the reaction mixture shows **8** as the main product (besides **3**) but in addition, homologous species $CH_3C_6H_3S_n$ with $n = 5-11$ can be detected. Once again the retention data prove the existence of a homologous series since

$$\ln k' = 0.2591 \cdot n - 0.7088$$

(correlation coefficient $r = 0.999$; eluent: CH_3OH; $n = 5-11$; t_o = 1.390 min). The retention indices of these species are given in Table 1; **8** forms deep-yellow, odorless crystals of m.p. 84.5 °C which are stable at 20 °C in air. The EI mass spectrum of **8** shows the molecular ion peak at m/z = 314 (base peak: $M^+ - S_4$), and the ^{1}H-NMR spectrum exhibits signals at δ = 2.42 (s, 3H), 7.24 (dq, J = 8, 1 Hz, 1H), 7.55 (q, J = 1 Hz, 1H), and 7.63 (d, J = 8 Hz, 1H) for the CH_3 and C_6H_3 units. In the Raman spectrum of solid **8** the S–S stretching vibrations give rise to a broad cluster of lines in the region of $\tilde{\nu}$ = 400–500 cm^{-1} from which two strong lines at $\tilde{\nu}$ = 463 and 491 cm^{-1} are sticking out. The strongest Raman lines occur at $\tilde{\nu}$ = 205 and 148 cm^{-1} and may be assigned to S–S–S bending modes by a comparison with the Raman spectrum of S_8[12].

The synthesis, properties, and spectra of the novel cyclic heptasulfanes **7** and **8** indicate that the molecular structures are as shown.

Scheme 1



7 **8**

These heterocycles decompose on electron impact to give S_4 and the trisulfane cations which are responsible for the base peaks in the mass spectra of **7** and **8**. The C_2S_7 rings of **7** and **8** may be compared to the homocyclic S_9 which exhibits C_2 symmetry according to density functional calculations[13] and Raman spectroscopy data[14]. In solution, however, it is to be expected that the sulfur-rich nine-membered rings undergo a pseudorotation (torsional motion) which, for instance, will make the protons of $C_2H_4S_7$ magnetically equivalent even when the solid-state structure should be of lower symmetry.

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Experimental

The preparations were carried out with carefully dried and distilled solvents; where necessary a protecting argon or nitrogen atmosphere was applied. SCl_2, S_2Cl_2, **1**[15], **6**[10], **9**[11] were prepared or purified by standard procedures; SO_2Cl_2, thiols and **4** were used as delivered. The HPLC[9] and Raman-spectroscopic equipment[16] has been described earlier; a DSC 7 calorimeter (Perkin-Elmer) was used for the thermal analysis. Routine mass and NMR spectrometers (Bruker WP 80) were used; NMR samples were dissolved in $CDCl_3$ or C_6D_6, and chemical shifts are given as δ values.

Bis(triphenylmethyl)pentasulfane (**5**): A solution of **4** (6.50 g, 23.3 mmol) in 40 ml of CS_2 was added to a slurry of **1** (4.95 g, 8.88 mmol) in 50 ml of CS_2 followed by stirring at 20°C for 48 h. After reducing the volume to 1/3 and filtering off the precipitated **3**, the mixture was separated by chromatography on silica gel $60F_{254}$ (Merck; column length 400 mm, diameter 33 mm, eluent CCl_4 and CS_2, flow 30 ml/min). The fractions containing **5** (as checked by HPLC) were collected, reduced in volume, and cooled to −24°C whereupon **5** crystallized. Recrystallization from $CHCl_3$/EtOH followed by heating of finely ground **5** in a vacuum ($\ll$ 1mbar) to 96°C for 15 min resulted in 4.76 g (83%) of **5** (colorless, rod-like, odorless crystals), m.p. 156°C (dec.) (ref.[8] 146−147°C). − ^1H NMR (80 MHz, $CDCl_3$): δ = 7.225 (30H). − ^{13}C NMR (80 MHz, $CDCl_3$; the numbering of C atoms starts with "a" at the tertiary atom and continues with "b" at the neighboring ring atom, etc.): δ = 73.741 (C^a), 127.225 (C^e), 127.936 (C^c), 130.338 (C^d), 143.179 (C^b); all signals broad-band decoupled.

$[(C_6H_5)_3C]_2S_5$ (646.96) Calcd. C 70.55 H 4.67
Found C 70.77 H 4.48

1,2,3,4,5,6,7-Heptathionane (**7**): A solution of **6** (1.45 g, 8.87 mmol) in 20 ml of CH_2Cl_2 was added within 20 min to 3.0 g (8.87 mmol) of **1**, suspended in 40 ml of CH_2Cl_2, and stirred at 20°C for 40 min. After reducing the solvent volume to one half in a vacuum, and filtering off the precipitated **3** (which was extracted with little CS_2), the solvents were evaporated completely in vacuo, and the residue was dissolved in as little CS_2 as possible. Chromatographic separation (silica gel $60F_{254}$, eluent CCl_4) and evaporation of the united solvents yielded a yellow oil which was dissolved in CS_2 (ca. 5 ml), mixed with 15 ml of $CHCl_3$ and 15 ml of C_2H_5OH, and stored at 20°C for 2 weeks. Crystallization could be supported by slow evaporation of the solvent. Yield: 0.7 g (31%) of **7**, yellow needles, m.p. 63°C, odorless. − ^1H NMR (80 MHz, $CDCl_3$): δ = 3.519 (s, 4H). − MS (70 eV, 70°C): *m/z* (%) = 252 (14) $[C_2H_4S_7^+]$, 188 (8) $[C_2H_4S_5^+]$, 156 (7) $[C_2H_4S_4^+]$, 124 (100) $[C_2H_4S_3^+]$, 92 (12) $[C_2H_4S_2^+]$, 60 (21) $[C_2H_4S^+]$.

$C_2H_4S_7$ (252.47) Calcd. C 9.51 H 1.60
Found C 9.54 H 1.51

9-Methyl-1,2,3,4,5,6,7-benzoheptathionine (**8**): The synthesis was performed by analogy with the preparation of **7** except that CCl_4 was used instead of CH_2Cl_2. Yield 1.8 g (60%) of **8**, deep-yellow, rhomboidal crystals, m.p. 84.5°C. − ^1H NMR (80 MHz, $CDCl_3$; for numbering of protons see Scheme 1): δ = 2.42 (CH_3), 7.24 (H^b), 7.55 (H^a), 7.63 (H^c); J_{CH_3,H^a} = 1 Hz, J_{CH_3,H^b} = 1 Hz, J_{H^c,H^b} = 8 Hz. − MS (70 eV, 60°C): *m/z* (%) = 314 (5) $[C_7H_6S_7^+]$, 250 (6) $[C_7H_6S_5^+]$, 218 (9) $[C_7H_6S_4^+]$, 186 (100) $[C_7H_6S_3^+]$, 154 (23) $[C_7H_6S_2^+]$, 122 (18) $[C_7H_6S^+]$.

$CH_3C_6H_3S_7$ (314.55) Calcd. C 26.73 H 1.92
Found C 27.01 H 1.87

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