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# A Simple Way of Synthesis of Bisethylthiopolymethylene Sulfides $EtS(CH_2S)_nEt$

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**Abstract**—Two methods of synthesis of bisethylthiopolymethylene sulfides $RS(CH_2S)_nR$ (R = Et, $n \geq 1$) are developed. Both approaches are based on the reductive cleavage of the S–S bonds in diethyl polysulfides or a mixture of diethyl polysulfides with elementary sulfur by the system: hydrazine hydrate–base. Subsequent alkylation of the formed thiolate anions with dichloromethane leads to the formation of mixtures of oligomeric bisethylthiopolymethylene sulfides with a predominance of compounds with $n$ = 1, 2.

Compounds of the type $RS(CH_2S)_nR$ ($n \geq 1$) are promising complexing agents and extractants of heavy metals, dopes for oils and fuels upgrading their antirust, anticuff, and anti-wear properties, as well as intermediate products in organic synthesis [1, 2]. However, they are hardly available synthetically. Until the present time only few bismethylthio polysulfides $MeS(CH_2S)_nMe$ ($n \leq 4$) have been described [3]. They were prepared in a low yield (not higher than 30%) in several stages basing on such hardly available compounds as methanethiol and bischloromethyl sulfide.

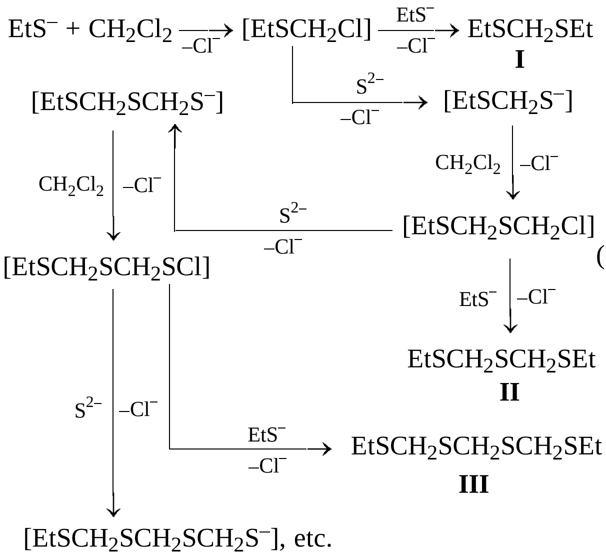
Now we propose two new approaches to the synthesis of $RS(CH_2S)_nR$ ($n \geq 1$) with R = Et which are based on the reductive cleavage of the S–S bonds in polysulfides and elementary sulfur.

In method *a* as starting reagents we used $Et_2S_m$, where $m$ = 3, 4. Their reduction with the system: hydrazine hydrate–base results in the formation of the following products:

$$4Et_2S_m + mN_2H_4 \cdot H_2O + 4mNaOH \longrightarrow 8EtSNa + 4(m-2)Na_2S + mN_2 + 5mH_2O. \quad (1)$$

As it follows from the stoichiometry of reaction (1), with $m$ = 3 1 mol of $S^{2-}$ ions is formed for each 2 mol of $EtS^-$ anions, and with $m$ = 4 per 2 mol of anions $S^{2-}$ for 2 mol of anions $EtS^-$ is formed.

In the course of alkylation with dichloromethane of the thiolate anions generated in reaction (1) the following consequtive transformations presented in Scheme (2) take place.



(2)

The formation of the mixture of products **I**–**III** and oligomers $EtS(CH_2S)_nEt$ with a hagher value of $n$ is controlled by the value of $m$ in the starting diethyl polysulfide. Diethyl polysulfides in reactions (1) and (2) can be used not only in the individual state, but also as a mixture of $Et_2S_2$, $Et_2S_3$, $Et_2S_4$, asf. The average sulfur content of this mixture governs the $m$ value of the polysulfide. These mixtures are easily prepared from elemental sulfur and alkyl halides in basic reducing systems [4].

Reaction of diethyl disulfide with dichloromethane in accordance with Scheme (2) leads to the formation of compound **I**, its content in the reaction mixture may amount to as much as 82% of the reaction products. Increasing the $m$ value to more than 2 results in the appearance of compounds **II**, **III** and others with different values of $n$ (see table).

Method *b* of synthesis of oligomers $EtS(CH_2S)_nEt$ is based on separate generation of anions $EtS^-$ (by the

Reaction conditions and yields of products $EtS(CH_2S)_nEt$

| Starting sulfur reagents | Molar ratio of starting reagents[a] | Conversion of $Et_2S_2$, % | Composition of reaction products, as by GLC | | |
|---|---|---|---|---|---|
| | | | **I** | **II** | oligomers ($n > 2$) |
| | | Method *a* | | | |
| $Et_2S_{2.5}$ | $Et_2S_{2.5} : NaOH : CH_2Cl_2 = 1:2.5:1.5$ | 80 | 37 | 14 | 12 |
| $Et_2S_{3.1}$ | $Et_2S_{3.1} : NaOH : CH_2Cl_2 = 1:3.5:2$ | 75 | 28 | 22 | 18 |
| | | Method *b* | | | |
| $Et_2S_2$ | $Et_2S_2 : NaOH : CH_2Cl_2 = 1:2:1$ | 98 | 82 | Traces | — |
| $Et_2S_2$; S | $Et_2S_2 : S : NaOH : CH_2Cl_2 = 1:0.5:4:0.5$ | 68 | 34 | 26 | 20 |
| $Et_2S_2$; S | $Et_2S_2 : S : NaOH : CH_2Cl_2 = 1:0.5:4:0.5$[b] | 87 | 40 | 18 | 18 |
| $Et_2S_2$; S | $Et_2S_2 : S : NaOH : CH_2Cl_2 = 1:1:6:1$[b] | 88 | 26 | 26 | 31 |

[a] Hydrazine hydrate was used as a medium solvent. [b] Separate preparation of solutions of sulfur and sodium ethanethiolate.

reductive activation of $Et_2S_2$ by the system: hydrazine hydrate–base) and anions $S^{2-}$ (with the use of reductive activation of elementary sulfur).

$$2Et_2S_2 + 4NaOH + N_2H_4 \cdot H_2O \longrightarrow 4EtSNa + N_2 + 5H_2O, \quad (3)$$

$$S_8 + 16NaOH + 4N_2H_4 \cdot H_2O \longrightarrow 8Na_2S + 4N_2 + 20H_2O. \quad (4)$$

Reaction mixtures prepared according to Schemes (3) and (4) were combined and subjected to the reaction with dichloromethane. The reaction proceeds by Scheme (2), as in the case of the first method (see table). However, synthesis of oligomers $EtS(CH_2S)_nEt$ with a high value of *n* by method *b* is more controllable. The necessity for the solutions of ethyl thiolate and sodium sulfide to be prepared separately stems from the fact that, when combined, sulfur and ethyl thiolate react to produce diethyl disulfide, even in the presence of such powerful reducing agent as hydrazine.

$$S_8 + 2EtS^- \longrightarrow Et_2S_2 + S_8^{2-}. \quad (5)$$

Under these conditions a major portion of diethyl disulfide does not enter reaction (2).

By vacuum distillation of the products of reaction (2) without the use of a superhigh vacuum only compounds **I, II** can be isolated. Higher oligomers appear to be unstable and decompose in the course of distillation. The earlier described in the literature oligomer $RS(CH_2S)_nR$ (R = Me, $n = 4$) was isolated at $10^{-3}$ mm Hg with the boiling point of 128° [3].

By means of GLC and GC-MS we fixed the formation by reaction (2) in appreciable amounts of no fewer than 5 oligomers. The organic layers obtained by the performance of synthesis by both methods contain the starting $Et_2S_2$, despite the quantitative proceeding of the reaction (3) (20–30% with the use of method *a* and 10–15% in the case of method *b*). It seems likely that $Et_2S_2$ is formed in the course of reactions (2)–(4) because of the presence of sulfur both in the separate preparation of the ethyl thiolate anion and the solution of sulfur (method *b*) and in the reduction of diethyl polysulfides in the basic reductive system. Dissolution of sulfur in the system: hydrazine hydrate–base, in addition to the formation of monosulfide anions [reaction (4)], can also lead to the generation of disulfide anions.

$$S_8 + 8NaOH + 2N_2H_4\_H_2O \longrightarrow 4Na_2S_2 + 2N_2 + 10H_2O. \quad (6)$$

Disulfide anions also can oxidize ethyl thiolate anions into diethyl disulfide.

$$S_2^{2-} + 2EtS^- \longrightarrow Et_2S_2 + S^{2-}. \quad (7)$$

In all cases 3,5-dithiaheptane (**I**) is formed with the highest yield, because in the process termination of the chain takes place. The highest yield of 3,5,7-trithianonane (**II**) is achieved with the use in reaction (2) of excess sulfur and methylene chloride.

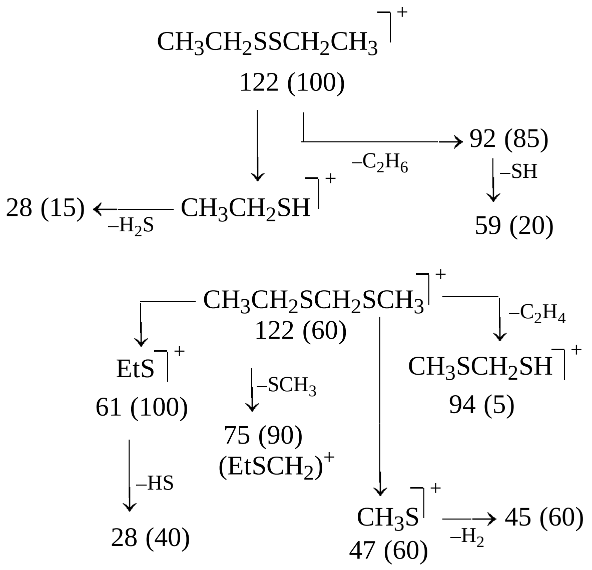
A careful analysis of the organic phase of the reaction mixtures by means of GLC and GC-MS revealed in some cases the formation in small proportions of the following reaction products: $EtSCH_2SMe$ (**IV**) (~1%) and $EtSCH_2SSEt$ (**V**) (~3%). These compounds are most likely the products of redox reactions proceeding in the used basic reductive system.

$$\mathrm{EtSCH_2SCH_2Cl} \xrightarrow[-\mathrm{HCl}]{[\mathrm{H}]} \underset{\textbf{IV}}{\mathrm{EtSCH_2SCH_3}},$$

$$\mathrm{EtS^-} + \mathrm{S_2^{2-}} \longrightarrow \mathrm{EtSS^-} + \mathrm{S^{2-}},$$

$$\mathrm{EtSCH_2SCH_2Cl} + \mathrm{EtSS^-} \longrightarrow \underset{\textbf{V}}{\mathrm{EtSCH_2SSEt}}.$$

Isomeric compounds **IV** and $Et_2S_2$ differ in the retention times in GLC analysis and the direction of fragmentation in the mass spectra [in the scheme given are the values of *m/z* ($I_{rel}$, %)].



As the length of the oligomeric chain grows, the intensity of the molecular ion peaks in the mass spectra drops steeply. The intensity of the molecular ion peak of compound **I** is 80%, and that of compound **II** is 20%, while for compound **V** it is only 2%. In the mass spectra of higher oligomers no peaks of molecular ions is observed. However, the presence of the fragmentation ions peaks 75 ($EtSCH_2^+$) ($I_{rel}$ 100%), 107 ($EtSCH_2S^+$) ($I_{rel}$ up to 30%), 121 ($EtSCH_2SCH_2^+$), and 153 ($EtSCH_2SCH_2S^+$) support the conclusion that higher oligomers $EtS(CH_2S)_nEt$ are present in heavier products of reactions (2).

The mixtures of oligomers $EtS(CH_2S)_nEt$ obtained by reaction (2) can be used without separation as extractants of heavy metals and as sulfurizing agents for oxide catalysts.

It can be thus stated that the proposed ways of preparation of oligomeric polymethylenesulfides $RS(CH_2S)_nR$ are characterized by the simplicity of their accomplishment and are based on the use of simple starting reagents, namely, elementary sulfur, dialkyl disulfides, and methylene chloride. Compound **I** or mixtures of oligomers are prepared in one preparative stage, and the oligomers can be separated by high-vacuum distillation.

## EXPERIMENTAL

The reactions progress and purity of the isolated products were monitored by GLC on a LKhM-80-MD chromatograph (column 2000 × 3 mm packed with 5% of silicone XE-60 on Chromaton N-AW-HMDS), carrier gas helium, linear programming of temperature at a rate of 12 deg/min.

The GC-MS analyses were performed on a chromatomass spectrometer AHP-GC-MS-5972 (capillary column 50 m × 0.2 mm × 0.5 μm, PONA, carrier gas helium, linear programming of temperature at a rate of 12 deg/min).

The NMR spectra were registered on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$ solutions with HMDS as an internal reference.

**Bisethylthiopolymethylene sulfides $EtS(CH_2S)_n \cdot Et$.** *a*. Into a flask equipped with a stirrer, reflux condenser, thermometer, and a dropping funnel an appropriate amount of alkali was placed, hydrazine hydrate was added as a solvent, and the mixture was heated to 50°C. At this temperature diethyl disulfide was added into the reaction mixture by portions. The reaction mixture was kept for 1 h at 80–90°C, cooled, and at 20–25°C dichlomethane was added by portions. After the completion of alkylation the reaction mass was kept at 60–70°C for 1 h, and cooled. The reaction products were extracted with dichloromethane, the extract was dried with $CaCl_2$. The solvent was evaporated, and the residue was analyzed and subjected to rectification in vacuo. The reaction conditions and the results are presented in the table.

**3,5-Dithiaheptane (I)** constitutes the major portion of the fraction bp 75–90°C (40 mm). After second distillation a practically pure product, bp 52°C (3 mm) was isolated. $^1H$ NMR spectrum, δ, ppm: 1.26 t ($CH_3$), 2.65 q ($SCH_2C$), 3.82 s ($SCH_2S$).

**3,5,7-Trithianonane (II).** bp 103°C (2 mm). $^1H$ NMR spectrum, δ, ppm: 1.25 t ($CH_3$), 2.65 q ($SCH_2C$), 3.81 s ($SCH_2S$), the ratio of intensities 3 : 2 : 2. With further rise in the distillation temperature there is observed a profound decomposition of the still residue. In the $^1H$ NMR spectrum of the residue in the weak field there are found three singlet signals 4.02, 3.95, and 3.81 ppm with the ratio of intensities of 1 : 2 : 5.

*b*. A solution of sodium ethanethiolate was prepared by method , and then finely powdered sulfur was added. The reaction mixture was kept for 1 h at 80–90°C, and then treated as described above for method *a*.

In the separate preparation of solutions of sulfur and sodium ethanethiolate sulfur solution was prepared by the procedure described in [4]. The obtained solutions were placed into a common vessel, the reaction mixture was kept for 1 h at 80–90°C, and then treated as in method *a*. The reactions conditions and the yields of oligomers are given in the table.

## ACKNOWLEDGMENTS

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