Reactions of Bielectrophiles (ClCH₂CH₂)₂Y with Sulfur in Basic Reducing Systems

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Received May 29, 2000

Abstract—A simple procedure was developed for preparing $bis(\beta$ -mercaptoethyl) ether and $bis(\beta$ -mecraptoethyl) sulfide from commercially available chemicals: elemental sulfur, alkali, and $bis(\beta$ -chloroethyl) ether or sulfide, based on thiylation with elemental sulfur of these substrates in the aqueous system hydrazine hydrate– alkali, with initial formation of the corresponding polysulfide polymers (thiokols). Their reduction with the system hydrazine hydrate–alkali, followed by acidification of dithiolate anions, yields the corresponding dithiols. Thiokols based on $bis(\beta$ -chloroethyl) ether are soluble in organic solvents; they were studied by ¹H NMR.

We have shown previously that 1,2-dichloroethane reacts with sulfur in the system NaOH–N₂H₄·H₂O– H₂O to form thiokol {SCH₂CH₂S]_n, which is subsequently reduced in the system hydrazine hydrate–alkali to the corresponding bisthiolate anion. Treatment of the latter with HCl yields 1,2-ethanedithiol [1]. The system hydrazine hydrate–alkali readily cleaves both cyclic S₈ molecules to give polysulfide anions S_n^{2–} (n = 1-4) [2] and the S–S bond in organic disulfides R₂S₂ to give thiolate anions RS[–] [3].

In view of the fact that organic dithiols are precursors of macrocyclic thiocrown ether systems [4], we performed the reactions of sulfur in the basic reducing systems with bielectrophiles $(\text{ClCH}_2\text{CH}_2)_2\text{Y}$ (Y = O, S) (**Ia**, **Ib**) with the aim to prepare the corresponding dithiols. Furthermore, transformations of **Ib**, which is a war gas (yperite), may open up new possibilities for its utilization.

We found that both compounds **Ia** and **Ib** readily react with a solution of sulfur in the system aqueous hydrazine hydrate–alkali with complete conversion and formation of polymeric polysulfides **II** of thiokol type:

$$S_8 + 8MOH + 2NH_2NH_2 \cdot H_2O$$

$$\rightarrow 4M_2S_2 + 2N_2 + 9H_2O, \qquad (1)$$

$$ClCH_{2}CH_{2}YCH_{2}CH_{2}Cl + M_{2}S_{2}$$

$$Ia, Ib$$

$$\xrightarrow{-2MCl} \{SCH_{2}CH_{2}YCH_{2}CH_{2}S\}_{n}, \qquad (2)$$

$$IIa, IIb$$

$$M = K$$
, Na; $Y = O(a)$, S(b).

Polymers IIa are viscous oily substances readily soluble in chloroform. This fact allowed us to study for the first time the ¹H NMR spectra of polysulfide polymers prepared by thiylation of bielectrophiles with polysulfide anions. The ¹H NMR spectrum of polymers **IIa** contains two groups of signals. A downfield multiplet centered at 3.74 ppm corresponds to the overlapping signals of the CH₂-Cl and CH₂-O protons, present also in the initial ether Ia (multiplet centered at 3.71 ppm). In the upper field, there are three triplets which, basing on data in [5], were assigned as follows (ppm): 2.61, to CH_2S-C ; 2.89, to CH_2S_2-C ; and 3.10, to CH_2S_3-C . These signals indicate that molecules of polymers IIa contain mono-, di-, and trisulfide units. The nature of polysulfide anions formed by dissolution of sulfur in the system aqueous hydrazine hydrate–alkali is determined by the ratio $MOH: S: N_2H_4$, and also by the dissolution conditions [3]. However, the system prepared by reaction (1) is undoubtedly characterized by the equilibrium

$$\mathbf{S}^{2-} \rightleftharpoons \mathbf{S}_2^{2-} \rightleftarrows \mathbf{S}_3^{2-} \rightleftarrows \mathbf{S}_n^{2-}. \tag{3}$$

In syntheses of polymers **IIa**, we took in all cases the ratio MOH : S 1 : 1, which should result in preferential formation of disulfides M_2S_2 . With 5 ml of hydrazine hydrate taken in reaction (1), the ratio of the S₁, S₂, and S₃ fragments in polymer **IIa**, according to the ¹H NMR spectrum, is 1 : 2 : 1. With 1 ml of hydrazine hydrate, this ratio changes to 1 : 1.7 : 1.7, i.e., equilibrium (3) is shifted to the right. In this case, alkylation with the equivalent amount of ether **Ia** should yield a polymer with a lower molecular weight. Analysis of the polymers for residual chlorine allowed evaluation of their molecular weight by the method of terminal groups [6]. Polymer **Ha** prepared in the presence of 5 ml of hydrazine hydrate has the molecular weight of ~1800, and that prepared in the presence of 1 ml of hydrazine hydrate, ~820.

Reaction (2) with sulfide **Ib** yields polymer **IIb**, which is insoluble in organic solvents. Its molecular weight is 4400. The properties of **IIb** resemble those of thiokols prepared by thiylation of dichloroethane with solutions of sulfur in the aqueous system hydrazine hydrate–MOH at the MOH: S ratio of 4:3.

$$S_{8} + 8MOH + 2N_{2}H_{4} \cdot H_{2}O$$

$$\rightarrow 2M_{2}S + 2M_{2}S_{2} + 2N_{2} + 9H_{2}O, \qquad (4)$$

$$M_{2}S_{1.5}$$

$$\text{ClCH}_2\text{CH}_2\text{Cl} + \text{M}_2\text{S}_{1.5} \xrightarrow[-2\text{MCl}]{} \text{IIc}$$
(5)

The molecular weight of the resulting polymer **IIc** is \sim 4200.

Polymers **IIa** and **IIb** were reduced in the system hydrazine hydrate–alkali to thiolates **IVa** and **IVb**, with the aim of subsequent preparation of the corresponding thiols **IIIa** and **IIIb** and their derivatives.

$$2\mathbf{IIa}, \mathbf{IIb} + 4nMOH + nN_2H_4 \cdot H_2O$$

$$\rightarrow 2nMSCH_2CH_2YCH_2CH_2SM + nN_2 + 5H_2O. \quad (6)$$

IVa, **IVb**

Mild acidification of dithiolates **IVa** and **IVb** formed by scheme (6) yielded dithiols **IIIa** and **IIIb**:

IVa, **IVb** +
$$2H^+ \xrightarrow{-2M^+} HSCH_2CH_2YCH_2CH_2SH.$$
 (7)
IIIa, **IIIb**

The yields of dithiols **IIIa** and **IIIb** are low: 25 and 34%, respectively. This may be due to the presence in polymer chains of the sulfide fragments $-CH_2CH_2$ -SCH₂CH₂- (owing to participation of monosulfides M₂S in the polycondensation), which are not noticeably reduced under conditions of reaction (6). Furthermore, in the course of reduction of **IIa** the arising dithiolate **IVa** partially undergoes intramolecular cyclization to 1,4-oxathiane **V** (yield up to 20%). Dithiolate **IVb** does not undergo heterocyclization to 1,4-dithiane under similar conditions.

Dithiols **IIIa** and **IIIb** are colorless liquids. Their IR spectra contain medium-intensity bands corresponding to the S–H vibrations (2556 and 2545 cm⁻¹, respectively). The other bands are assigned in the Experimental.

Dithiolate anions **IVa** formed by reduction of **IIa** were alkylated with ethyl bromide, and products **VIa** were isolated and characterized.

$$IVa + C_2H_5Br \longrightarrow EtSCH_2CH_2OCH_2CH_2SEt.$$
 (8)
VIa

Dithiol **IIIb** is also formed by reduction of polymer **IIc** obtained by scheme (5) from dichloroethane (yield 37%). 1,2-Ethanedithiol is formed simultaneously in approximately the same yield. At the same time, reduction of the polymer prepared by scheme (2) from yperite yields only traces (<1%) of 1,2-ethane-dithiol.

Formation of dithiol **IIIb** from the polymer prepared by schemes (4)–(7) from dichloroethane suggests regular alternation of di- and monosulfide units in **IIc** (see below):

Decrease of the MOH : S ratio in reaction (4) to 1 : 1 and 1 : 1.5 favors generation of M_2S_2 and M_2S_3 and formation of polymers based on dichloroethane [scheme (5)] with disulfide and trisulfide units. Subsequent reduction of these polymers leads to sharply increased (to 75%) yield of ethanedithiol [1] and to decreased yield of dithiol **IIIb** (5% or traces).

The polymer **IIc** prepared by reaction (5) from dibromoethane is a viscous rubbery product with the molecular weight of \sim 3500. Its reduction by reactions (6) and (7) mainly yields 1,2-ethanedithiol; its yield

does not exceed 33%, with dithiol **IIIb** formed only in trace amounts.

We have shown previously [7] that in reactions with chalcogenide anions Y_n^{2-} (Y = S, Se, Te) in hydrazine hydrate organyl chlorides are more reactive than the corresponding organyl bromides and even iodides. Therefore, different reactivity of 1,2-dichloroethane and 1,2-dibromoethane in thiylation in basic reducing media is due to the fact that dichloroethane reacts equally fast with the anions S^{2-} , S_2^{2-} , etc., whereas dibromoethane, probably, first

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selectively reacts with di- and polysulfide anions to form a polymer with di- and trisulfide units. After exhaustion of polysulfide anions, further chain propagation occurs at the expense of S^{2-} anions, and the structure of the resulting polymer will be as follows:

Reduction of such macromolecular chain yields no dithiol **IIIb**.

Thus, we have developed a simple route to such dithiols as bis(2-mercaptoethyl) ether **IIIa** and bis(2-mercaptoethyl) sulfide **IIIb**, based on simple commercially available chemicals: elemental sulfur, alkali, ether **Ia**, and sulfide **Ib**. Thiylation with elemental sulfur of **Ia** or **Ib** in the aqueous system hydrazine hydrate–alkali yields the corresponding polysulfide polymers, thiokols. Their reduction with the system hydrazine hydrate–alkali, followed by acidification of the resulting thiolate anions, yields the corresponding dithiols **IIIa** and **IIIb**. Dithiol **IIIb** can also be prepared from thiokol **IIc** synthesized from dichloroethane and a sulfur solution at MOH : S 2 : 1.5.

EXPERIMENTAL

The IR spectra were recorded on an IF-525 Sample Scant-250 spectrometer (thin films for liquids and KBr pellets for solids).

The ¹H NMR spectra were recorded on a Jeol FX-90Q spectrometer (90 MHz) from 15-20% solutions in CDCl₃ or CCl₃F.

The GC–MS analysis was performed with a GC–MS-5972 AHP device (50 m \times 0.2 mm \times 0.5 μ m capillary column, PONA, carrier gas He, linear heating rate 12 deg min⁻¹).

The reaction progress was monitored and the product purity checked with an LKhM-80MD chromatograph (2000 × 3-mm column, stationary phase 5% Silicone XE-60 on Chromaton N-AW-HMDS, carrier gas He, linear heating rate 12 deg min⁻¹).

Polymer IIa. A three-necked flask equipped with a stirrer, a reflux condenser, a thermometer, and a unit for loading reactants was charged with 4 g of NaOH (or 5.6 g of KOH), 30 ml of water, and 5 ml of hydrazine hydrate, and 3.2 g of sulfur was added in portions with stirring. After the added sulfur dissolved, the mixture was stirred for 1 h at 90°C and then cooled, and 7.15 g of **Ia** was added in portions at $20-25^{\circ}$ C. The mixture was heated for 1 h at 80°C and

then cooled, and the resulting polymer was extracted with chloroform. The organic layer was dried over CaCl₂, the solvent was removed in a vacuum, and the residue was dried. Yield of **Ha** 62%. IR spectrum, v, cm⁻¹: 2930, 2905, 2890, 2850 [v(C–H)]; 1465, 1450, 1405, 1350 [δ (CH₂)]; 1280, 1100 [v(C–O)]; 750 (C–S); 470 (S–S). For the ¹H NMR spectrum, see text. Found, %: C 34.61; H 5.88; S 48.33: Cl 4.02. Calculated for the formula of **Ha**, %: C 35.29; H 5.88; S 47.06.

With 1 ml of hydrazine hydrate and equal other conditions, the yield of **Ha** was 67%. Found, %: Cl 8.62; S 41.18. $C_{24}H_8Cl_2O_6S_{10}$. Calculated, %: Cl 8.63; S 38.88.

Polymer IIb. A sulfur solution was prepared as described above, and 7.8 g of **Ib** was added. The mixture was kept for 2 h at 90–100°C. After cooling, the polymer (white powder) was filtered off, washed with water and ethanol, and dried. Yield of **IIb** 76%; mp 90–100°C (with decomposition). IR spectrum, v, cm⁻¹: 2930, 2905, 2890, 2850 [v(C–H)]; 1465, 1450, 1405, 1350 [δ (CH₂)]; 810, 750 (C–S); 471 (S–S). Found, %: S 62.57: Cl 1.59. Calculated for polymer **IIb**, %: S 63.16.

Polymer IIc. *a*. A sulfur solution was prepared from 4 g of NaOH, 30 ml of water, 5 ml of hydrazine hydrate, and 2.4 g of sulfur, and 4.95 g of dichloroethane was added in portions. The mixture was stirred for 1 h at 90°C; after cooling, polymer **IIc** was filtered off. Yield 83%; mp 95–100°C (with decomposition). Found, %: S 61.06: Cl 1.62. Calculated for **IIc**, %: S 63.16.

b. Under similar conditions but at the molar ratio NaOH: S 2:3, a rubbery polymer was obtained in 98% yield. Found, %: S 75.38: Cl 1.96. Calculated for $\{SCH_2CH_2SS\}_n$, %: S 77.42. $M \sim 3600$.

c. A sulfur solution was prepared under similar conditions but at the ratio KOH : S 4 : 3, and 9.36 g of 1,2-dibromoethane was added. The white rubbery polymer was filtered off, washed with water and ethanol, and dried. Yield 62%. Found, %: S 64.51: Br 4.54. Calculated for **IIc**, %: S 63.16.

3-Oxapentane-1,5-dithiol IIIa. A 2.4-g portion of NaOH was dissolved in 20 g of hydrazine hydrate, and 3.5 g of thiokol IIa was added. The mixture was stirred for 3 h at 80–90°C. After cooling, the mixture was poured under argon onto ice (200 g) containing 45 ml of concentrated HCl. Dithiol IIIa was extracted with ether, the extract was dried over $MgSO_4$, the solvent was removed in a vacuum, and the residue was vacuum-distilled. The fraction with bp 80-81°C (10 mm Hg) was practically pure dithiol IIIa. Yield 25%. IR spectrum, v, cm⁻¹: 2936, 2914, 2886, 2854 [ν(C–H)]; 2557 [ν(S–H)]; 1454, 1417, 1357 [δ(CH₂)]; 1103 [v(C–O)]; 760 (C–S). ¹H NMR spectrum, δ , ppm: 1.60 t (SH), 2.69 m (S-CH₂), 3.60 t (O-CH₂). 1,4-Oxathiane V is present in the first fraction from isolation of IIIa; bp 40°C (10 mm Hg) [8]. The IR spectrum contains the bands $v(CH_2)$ and $\delta(CH_2)$. ¹H NMR spectrum, δ , ppm: 2.65 t (SCH₂), 3.65 t (OCH₂). Mass spectrum, m/z (I_{rel} , %): 104 (90) [M^+], 74 (30) $[M - CH_2O]^+$, 61 (70) $[M - CH_2CHO]^+$; 46 (95) $[CH_2S]^+$; 27 (100) $[CH_2CH]^+$.

3-Thiapentane-1,5-dithiol IIIb was prepared similarly from **IIb**. Yield 34%; bp 115°C (5 mm Hg) [9]. IR spectrum, cm⁻¹: 2934, 2918, 2846 [v(C–H)], 2545 [v(S–H)], 1426 [δ (CH₂)]; 765 (C–S). ¹H NMR spectrum, δ , ppm: 1.72 t (SH), 2.76 m (S–CH₂).

6-Oxa-3,9-dithiaundecane VIa. A 2.4-g portion of NaOH was dissolved in 20 g of hydrazine hydrate, and 4 g of thiokol **IIa** was added. After dissolution of the thiokol, 6.54 g of ethyl bromide was added in portions. The mixture was stirred for 1 h at 70°C. The organic products were extracted with ether, the extract was washed with water and dried over CaCl₂, the solvent was distilled off, and the residue was vacuum-distilled. Yield of **VIa** 1.45 g (30%); bp 100°C (3 mm Hg). Found, %: C 50.02; H 9.24; S 33.07. C₈H₁₈OS₂. Calculated, %: C 49.48; H 9.28; S 32.99. ¹H NMR spectrum, δ, ppm: 1.25 t (CH₃), 2.62 m

(SCH₂), 3.62 t (OCH₂). Mass spectrum, m/z (I_{rel} , %): 165 (80) $[M - C_2H_5]^+$, 133 (15) $[M - SC_2H_5]^+$, 89 (100) $[M - C_2H_5SCH_2CH_2]^+$; 88 (90) $[-CH_2CH_2S-CH_2CH_2-]^+$, 75 (40) $[C_2H_5SCH_2]^+$, 61 (75) $[C_2H_5S]^+$.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32810a).

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