CONCLUSIONS

3,6-Di-tert-butylpyrocatechol forms 3,4-dibromo-6-tert-butylpyrocatechol on bromination. Protection of one or both hydroxyl groups allows a classical electrophilic substitution to be carried out.

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SYNTHESIS AND DEHYDRATION OF BIS(2-HYDROXYALKYL) SULFIDES

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The dehydration of 1,5-alkanedioles proceeds in good yield to form alkyl-substituted tetrahydropyrans [1]. It was thus of interest to study the dehydration of bis(2-hydroxyalkyl) sulfides with the aim of preparing alkyl-substituted 1,4-oxathianes. Bis(2-hydroxyalkyl) sulfides, previously obtained from the reaction of alkene chlorohydrins with Na₂S [2], or of alkene oxides with HSCH₂CH₂OH [3], were synthesized by us using a modification of the method given in [3]. We replaced C₂H₅ONa by methanolic KOH, affording a higher yield of the desired product (Table 1).

The dehydration of bis(2-hydroxyalkyl) sulfides has been little studied. Information is available on the dehydration of bis(2-hydroxyethyl) sulfide [4] and 2-methyl-1-(2-hydroxy-ethylthio)-3-buten-2-ol [5].

This investigation concerns the dehydration of 2-hydroxyethyl-2'-hydroxyhexyl sulfide (I), 2-hydroxyethyl-2'-hydroxyoctyl sulfide (II), 2-hydroxyethyl-2'-hydroxyclohexyl sulfide (III), and bis(2-hydroxyhexyl) sulfide (IV). The reactions were carried out by boiling the bis(2-hydroxyalkyl) sulfides in toluene in the presence of p-toluenesulfonic acid while distilling off the water. One mole of water was obtained per mole of compounds (I)-(III), whereas two moles of water were obtained per mole of compound (IV). The dehydration of all the bis(2-hydroxyalkyl) sulfides we studied under the conditions described yielded, on distilling the toluene, viscous liquids, evidently comprising the products of linear polycondensation. Thus, for example, the product formed by the dehydration of compound (II) had an average molecular weight* of 376, and an elemental analysis corresponding to the empirical formula $C_{10}H_{20}OS$. The IR spectrum of this compound had a strong absorption band at 1105 cm⁻¹

*Determined cryoscopically in benzene.

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TABLE 1. Constants and Elemental Analysis of Bis(2-hydroxyalkyl) Sulfides

Com- pound	Yield	bp, °C (p, mm Hg)	d ²⁰ 4	n_{D}^{20}	Found, %			Empirical	Calculated, %		
					С	н	s	formula	С	н	s
(I) (II) (III)[3] (IV)	98,3 92,4 98,0 43,3	164 – 165 (6) 157–159 (1) mp 45–45,5 174–176(1)	1,0418 1,0080 0,9525	1,4960 1,4920 1,4880	$53, 58 \\ 58, 23 \\ 54, 50 \\ 61, 32$	10,10 10,46 9,26 11,24	17,87 15,40 18,15 13,88	$\begin{array}{c} C_8H_{18}O_2S\\ C_{10}H_{22}O_2S\\ C_8H_{16}O_2S\\ C_{12}H_{26}O_2S \end{array}$	53,93 58,25 54,54 61,54	10,11 10,68 9,09 11,11	17,97 15,53 18,18 13,67

TABLE 2. Constants and Elemental Analysis of the Dehydration Products of Bis(2-hydroxyalkyl) Sulfides

Com- pound	Yield, %	bp, °C (p, mm Hg)	d420	n_{D}^{20}	Found, %			Empirical	Calculated, %		
					С	н	s	formula	С	н	s
(V) (VI) (VII) (VIII)	21,8* 15,9* 17,2* 50,5	84,585,5(5) 120122(7) mp 3838,5 103,5106,5(3)	0,9778 0,9688 0,8850	1, 486 5 1,4870 1,4870	60,30 63,78 60,54 72,97	10,13 10,57 8,80 11,18	19,78 17,07 19,89 15,84	$\begin{array}{c} C_8 H_{16} OS \\ C_{10} H_{20} OS \\ C_8 H_{14} OS \\ C_{12} H_{22} S \end{array}$	$60,00 \\ 63,83 \\ 60,76 \\ 72,72$	10,00 10,63 8,86 11,11	20,00 17,02 20,25 16,16

*In addition to compounds (V), (VI), and (VII), the dehydration products include 1,4-dithiane in yields of 48.7, 60.7, and 38.1%, respectively. Calculation indicates that 1 mole of 1,4-dithiane is obtained from 2 moles of bis(2hydroxyalky1) sulfide.

TABLE 3. Mass Spectra of Products of Dehydration of Bis(2hydroxyalkyl) Sulfides (peak intensities as percent of the maximum)

m/e	Compound				Co	mpoun	d		Compound		
	(V)	(VI)	(VII)	m/e	(V)	(VI)	(VII)	m/e	(V)	(VI)	(VII)
$\begin{array}{c} 41\\ 43\\ 45\\ 46\\ 47\\ 54\\ 57\\ 60\\ 61\\ 62 \end{array}$	35. 5 12 ,0 100 10,2 17. 5 26 ,8	56,0 55,0 100 45,1 18,7 70,0 21,1	$\begin{array}{c} 3.5\\ 13.5\\ 14.0\\ 10.0\\ 5.0\\ 25.4\\ 18.5\end{array}$	67 69 71 74 75 77 81 83 85 89 97	16.1 3,0 86.7 25,0 11.8 50,1	20,0 8,0 90,0 35.6 8,5 20,0 10.1	31,5 3.1 50,0 13,3 15.3	98 99 101 103 111 113 115 158 160 188	20,1 30,5 *	13,5 30,1 13,1 39,8 32,1 *	100 38,2 10.1 61,5 *

*Molecular ions.

characteristic of an ether linkage, and very weak absorption bands at 1300 cm^{-1} , indicating ring sulfur,* and at 3460 cm^{-1} , characteristic of hydroxyl.

Vacuum heating of the linear polycondensation products (I)-(III) led to their destruction, with the formation of the alkyl-substituted 1,4-oxathiane and 1,4-dithiane (Table 2). From the linear polycondensation product (IV) one obtains the diene sulfide.

The IR spectra of bis(2-hydroxyalkyl) sulfides (I)-(IV) contain absorption bands at 1030, 1055, 1075, 1295, and 3350-3370 cm⁻¹, characteristic of primary secondary alcohols. The IR spectra of the 1,4-oxathianes (V)-(VII), have absorption bands characteristic of ether linkages (1100-1120 cm⁻¹) and of S in six-membered rings (1300-1310 cm⁻¹). The IR spectra of the diene sulfide (VIII) has absorption bands at 970, 1655, and 3025 cm⁻¹, characteristic of unsaturated sulfides with β -trans double bonds [6].

*Oxidation of 2-butyl-1,4-oxathiane (V) to the corresponding sulfoxide resulted in the loss of the 1300 cm^{-1} absorption band in the IR spectrum.



The PMR spectra of 1,4-dithiane and 1,4-oxathiane were obtained in order to elucidate the PMR spectra of (V)-(VII). The spectrum of 1,4-dithiane has a methylene proton singlet (2.83 ppm). The spectrum of 1,4-oxathiane has a triplet for methylene protons on the carbons linked to sulfur (2.50 ppm) and a triplet for methylene protons in the carbons linked to oxygen (3.67 ppm). The PMR spectra for compounds (V)-(VII) are given in the experimental part of this paper.

The fragmentation of 1,4-oxathiane under electron impact was studied in [7]. The alkyl substituents in compounds (V) and (VI) scarcely affect the molecular ion intensity [30.5 and 32.1% for (V) and (VI), respectively, and 34.6% for 1,4-oxathiane]. The molecular ion intensity for compound (VII) is almost twice as great (61.5%). One of the fragmentation paths of compound (V) is the removal of the alkyl radical with formation of an ion with the structure of 1,4-oxathiane (m/e 103), which in turn dissociates by the scheme postulated in [7]. Another fragmentation path is the removal of a C₂H₃OS radical forming the rearranged ion $[C_6H_{13}]^+$, which is the first member of the series $[C_nH_{2n+1}]^+$, $[C_nH_{2n-1}]^+$. With increasing length of the alkyl radical, as in compound (VI), the contribution of hydrocarbon ions to the mass spectrum increases. However, for compounds (V) and (VI), as well as for 1,4-oxa-thiane, the most intense peaks pertain to the sulfur-containing fragments: $[C_2H_4S]^+$ and $[CH_2S]^+$. A characteristic feature of the dissociation of the molecular ion of compound (VII)

is the rupture of a pair of bonds in the oxathiane and cyclohexane rings

1 c b a , lead-

ing to the formation of the following pairs of ions: a) m/e 98 and 60; b) m/e 81 and 77; c) m/e 101 and 57; d) m/e 115 and 43 (Table 3).

EXPERIMENTAL

IR spectra were obtained on a UR-20 spectrophotometer. Mass spectra were recorded on an MKh-1303 apparatus with an electron ionization energy of 70 eV, emission current of 1.5 mA, and ionization chamber temperature of 120°C. PMR spectra of products were obtained on a BS-487B (80 MHz) spectrometer, in CCl₄ solution at 26°C. The chemical shifts of the protons relative to hexamethyldisiloxane appears as ppm on the δ scale.

Synthesis of Bis(2-hydroxyalkyl) Sulfides (I)-(III). The syntheses were conducted using the following general procedure. To a stirred, snow-cooled solution of 0.05 mole of 85% KOH in 100 ml of methanol was added 0.5 mole of monothioethylene glycol and then, dropwise 0.5 mole of the alkene oxide. When the temperature of the mixture is raised to 15° C, an exothermic reaction occurs. After the exothermic reaction was complete, the mixture was boiled for 30 min, cooled, and saturated with CO₂; the K₂CO₃ was filtered off, and the filtrate distilled under vacuum.

Bis(2-hydroxyhexyl) sulfide was obtained from hexene chlorohydrin and Na₂S by a procedure analogous to that described for the synthesis of bis(2-hydroxyethyl) sulfide [2]. The yields, constants, and analytical data for the bis(2-hydroxyalkyl) sulfides are shown in Table 1.

Dehydration of Bis(2-hydroxyalky1) Sulfides. Dehydrations were conducted by the following general procedure. To a flask, equipped with a Dean-Stark trap, 0.1 mole of the bis(2hydroxyalky1) sulfide was added, along with 80 ml of toluene and p-toluenesulfonic acid

$$(S)_{S}, 2,83 \text{ s} (8 \text{ H}); \ b_{a} (S); 2,50 \text{ t} (4 \text{ H}^{a}, J = 5 \text{ Hz}); 3,76 \text{ t} (4 \text{ H}^{b}, J = 5 \text{ Hz});$$

 $\begin{array}{c} & \mathbf{C} \\ \mathbf{C} \\$

(4 H^c); 3,22-3,75 m (2 H^a); 3,78-4,20 m (1 H^b);
$$a = \begin{pmatrix} a & b & 0 \\ a & a & c & c \\ a & c & c & c \\ a &$$

 $2.07 - 2.68 \text{ m}(2\text{H}^{\text{e}}); 2.70 - 3.30 \text{ m}(2 \text{ H}^{\text{d}}); 3.40 - 3.75 \text{ m}(1 \text{ H}^{\text{c}}); 3.91 - 4.16 \text{ m}(1 \text{ H}^{\text{b}}).$

(equal to 1-2% of the weight of thiodiol). The solution was boiled until it ceased to evolve water (2-4 h). The mixture was cooled, washed with water, with a Na_2CO_3 solution, and again with water, and dried over MgSO₄. After distilling off the toluene, the residue was vacuum distilled (2 mm). Distillate slowly begins to appear at a bath temperature of 180-190°C. When the linear polycondensation products of (I) and (II) are distilled under vacuum, a liquid distillate is obtained, followed by 1,4-dithiane, mp 109.5-110°C (from ether) [8]. The residue is undistillable polymer. The liquid distillate was redistilled under vacuum to yield compounds (V) and (VI).

On vacuum distillation of the linear polycondensation product of (III), the distillate which slowly begins to form at 180-190°C crystallizes in the condenser. The crystals are of 1-oxa-4-thiabicyclo[4.4.0]decane (VII). A small amount of liquid distillate follows and, finally, 1,4-dithiane. The residue is undistillable polymer. The yields, constants, and elemental analysis of the products of dehydration of bis(2-hydroxyalkyl) sulfides are given in Table 2. Data from the PMR spectra are given above.*

CONCLUS IONS

1. As a result of modification of the conventional procedure, we obtained bis(2hydroxyalkyl) sulfides from alkene oxides and monothioethylene glycol with substantially increased yields of the desired product.

2. On dehydration of primary-secondary bis(2-hydroxyalkyl) sulfides, the corresponding 2-alkyl-1,4-oxathiane and 1,4-dithiane are formed. On the dehydration of di-secondary bis-(2-hydroxyalkyl) sulfides, however, the diene sulfide is formed.

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^{*}In the formula for the compound, protons having the same chemical shift are shown by the same letter designation.