O_3 per hour). The reaction mixture was poured into 3 mL of a 1 *M* solution of $Na_2S_2O_3$ and extracted with Et_2O (3×10 mL). The extract was successively washed with 10% Na_2CO_3 and a saturated solution of NaCl, dried with $MgSO_4$, and evaporated to give **2** or **2a** (0.24 g, 97.2%), n_D^{20} 1.4504 (for **2a** $[\alpha]_D^{20}$ −24.6° (liquid))[1] as individual compounds (GLC). IR, ν/cm^{-1}: 1700 (C=O).

B. An O_2/O_3 mixture was passed at a rate of 10 L h^{-1} through a solution of compound **1** (0.25 g) and $Co(OAc)_2 \cdot 4\ H_2O$ (0.005 g) in 10 mL of EtOAc at 20 °C for 1.5 h. The reaction mixture was then worked up as described in procedure *A*. The mixture containing product **2** (90%) and **3** (10%) (GLC analysis) was obtained in a total yield of 0.24 g. IR, ν/cm^{-1}: 1700 and 1715 (C=O).

The ozonolysis of menthol (1) in Freon-113. An O_2/O_3 mixture was passed at a rate of 10 L h^{-1} through a solution of compound **1** (0.25 g) and $Co(OAc)_2 \cdot 4\ H_2O$ (0.005 g) in 10 mL of Freon-113 at −30 to −40 °C for 1 h. Freon-113 was periodically added to maintain the initial volume. Then the reaction mixture was worked up as described above in procedure *A*. The mixture containing product **2** (95%) and the starting compound **1** (5%) (GLC analysis) was obtained in a total yield of 0.24 g. IR, ν/cm^{-1}: 1700 (C=O), 3350 br. (OH).

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Homolytic cyclization of 1,3-propanedithiol to 1,2-dithiolane in the presence of 2,5-dimethyl-2,4-hexadiene

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2,2-Diethyl-1,3-propanedithiol undergoes cyclization to 4,4-diethyl-1,2-dithiolane upon interaction with 2,5-dimethyl-2,4-hexadiene in benzene in the presence of azodiisobutyronitrile. The reaction proceeds according to the radical chain mechanism.

Key words: 2,2-diethyl-1,3-propanedithiol, cyclization, radical chain mechanism, 4,4-diethyl-1,2-dithiolane.

Conversions of thiols to disulfides are of great importance in synthetic organic chemistry as well as in biochemistry. A great number of works was devoted to studies of these conversions.[1]

Disulfides are generally synthesized by oxidation reactions, which proceed under the action of various oxidizing agents (for example, molecular oxygen,[2] Cu^{II} salts in the presence of oxygen,[3] halogens,[4,5] hypohalides,[6] sodium perborate,[7] potassium ferrate,[8] *etc.*) on thiols. For this purpose, electrochemical oxidation was also successfully used.[9,10]

Under the action of oxidizing agents, 1,3- and 1,4-dithiols were converted to five-membered and six-membered cyclic disulfides (1,2-dithiolanes and 1,2-dithianes), respectively.[11]

As part of continuing studies of free-radical processes with the participation of thiols, in particular, of their addition at multiple carbon—carbon bonds,[12,13] in

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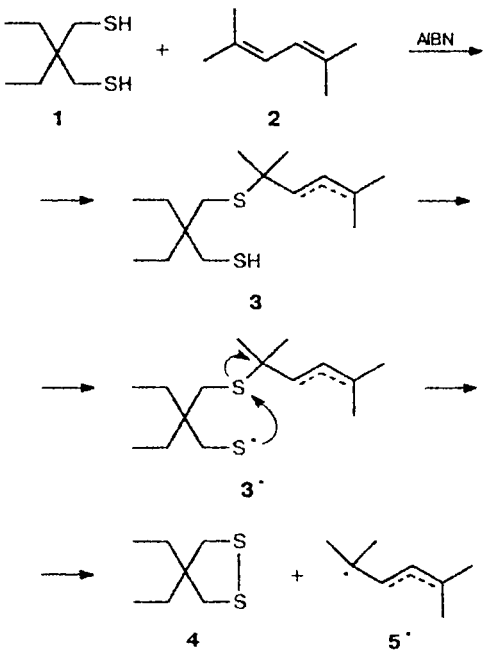
this work we found a new reaction of cyclization of 1,3-dithiols to 1,2-dithiolanes.

It was found that the reaction of 2,2-diethyl-1,3-propanedithiol (**1**) with 2,5-dimethyl-2,4-hexadiene (**2**) initiated with azodiisobutyronitrile (AIBN) gave cyclic disulfide, 4,4-diethyl-1,2-dithiolane (**4**), rather than the expected 1 : 1 addition product (**3**). When dithiol **1** and diene **2** were taken in a ratio of 1 : 1 and a 15% amount of AIBN (with respect to the reagents) was used (duration of the reaction in boiling benzene was 6 h), the yield of dithiolane **4** was 66% with respect to dithiol used (4.4 mol per mole of AIBN). In this case, the consumed diene **2** (80%) was completely converted to the oligomer. Dithiol **1** was also partially trapped in the course of oligomerization. A decrease in the amount of the initiator from 15 to 5% resulted in the increase in the yield of dithiolane from 4.4 to 11 mol per mole of AIBN. In the absence of diene **2**, dithiol **1** was also converted to dithiolane **4** under the action of AIBN, but its yield, according to the stoichiometry, was no more than one mole per mole of the initiator.

From the above-mentioned data it follows that the formation of dithiolane **4** in the presence of diene **2** proceeds according to the radical chain mechanism whose unit can be represented by Scheme 1.

Scheme 1



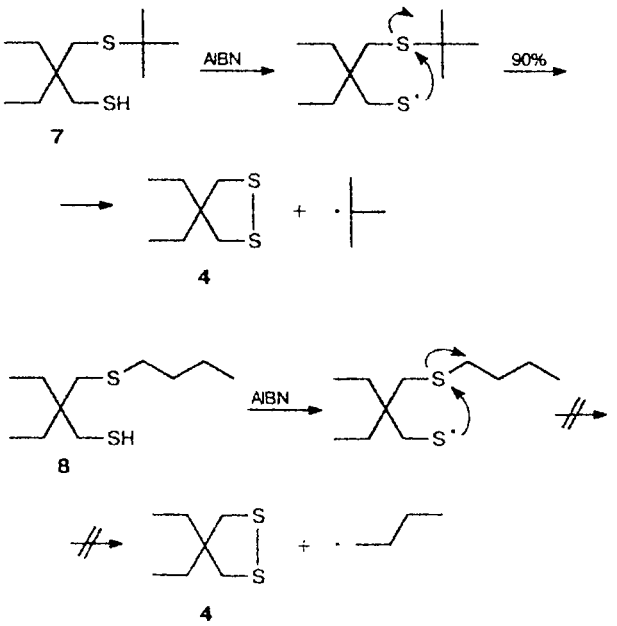
Evidently, the 1 : 1 adduct **3** was initially formed. Under the reaction conditions, compound **3** generated the thiyl radical **3'**, which underwent cyclization to dithiolane **4**.

The driving force for the stage of cyclization is homolytic substitution at the S atom in radical **3'** accompanied by elimination of the tertiary carbon-centered radical **5'**, which is, apparently, additionally stabilized through conjugation with the double bond. Radical **5'** is further involved in acts of transfer of the kinetic chain in the reaction of oligomerization of diene **2**.

The above-mentioned structural features that characterize the leaving radical **5'** appeared to be the necessary conditions for cyclization of thiol **3**. The replacement of the tetramethylbutenyl fragment containing the tertiary C atom at the S atom by the *n*-alkyl group led to the fact that the structurally changed thiol lost its ability to undergo cyclization to dithiolane **4**. Thus, the reaction of dithiol **1** with decene-1 initiated with AIBN proceeded with the formation of the 1 : 1 adduct, 3-decylthio-2,2-diethylpropanethiol (**6**), in 83% yield. *n*-Decane, which should be formed in the case of cyclization of adduct **6**, was not found in the reaction products. The amount of dithiolane **4** formed corresponded to the amount of AIBN consumed in the reaction.

The validity of the conclusion about the effect of the structure of the leaving radical on the process of homolytic cyclization of thiol **3** to dithiolane **4** was confirmed using two thiols, which are model compounds with respect to the 1 : 1 adducts of dithiol **1** with alkenes, as additional examples (Scheme 2). For this purpose, we carried out the reactions of AIBN with 3-*tert*-butylthio- (**7**) and 3-butylthio-2,2-diethylpropanethiol (**8**), which were prepared by the reaction of dithiolane **4** with *tert*-butylmagnesium chloride or *n*-butyllithium, respectively. Under the action of 2-cyanoisopropyl radicals generated from AIBN, thiol **7** containing the *tert*-butyl group was converted to thiolane

Scheme 2



4 in 90% yield. Thiol **8** containing the *n*-butyl group did not undergo cyclization.

Therefore, the free-radical reactions of 1,3-dithiols with olefins are accompanied by cyclization of the intermediate 1 : 1 adduct to 1,2-dithiolane if the tertiary C atom is involved in the formation of a new S—C bond. If the primary C atom is involved in this reaction, the 1 : 1 adduct does not undergo cyclization to 1,2-dithiolane.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in $CDCl_3$. The GLC analysis was carried out on a Varian-3700 chromatograph (2000×4-mm column with 5% SE-superphase on Inerton-N-AW 0.125×0.16; initial temperature 80 °C; final temperature 240 °C; rate of heating 12 K min^{-1}). The column chromatography was performed on silica gel L 40/100 (hexane as the eluent).

2,2-Diethyl-1,3-propanedithiol (1) was prepared from 2,2-diethylpropane-1,3-diol ditosylate under the action of Na_2S_2 in DMF followed by reduction with $LiAlH_4$,[11] b.p. 82—84 °C (10 Torr). ^{1}H NMR, δ: 0.75 (t, 6 H, CH_3CH_2, J = 7.6 Hz); 1.09 (t, 2 H, SH, J = 8.6 Hz); 1.33 (q, 4 H, CH_3CH_2, J = 7.6 Hz); 2.49 (d, 4 H, CH_2SH, J = 8.6 Hz).

3-Butylthio-2,2-diethylpropanethiol (8) was prepared by the reaction of a 2.5 *M* BuLi solution (0.63 mL, 1.57 mmol) with 4,4-diethyl-1,2-dithiolane (0.22 g, 1.34 mmol) in THF as described previously.[12] Compound **8** was obtained in a yield of 0.26 g (90%) as a colorless liquid. ^{1}H NMR, δ: 0.78 (t, 6 H, two CH_3CH_2 groups, J = 7.5 Hz); 0.90 (t, 3 H, CH_3, J = 7.3 Hz); 1.18 (t, 1 H, SH, J = 8.8 Hz); 1.33—1.45 (m, 2 H, $CH_2CH_2CH_3$); 1.36 (q, 4 H, two CH_2Me groups, J = 7.5 Hz), 1.50—1.64 (m, 2 H, SCH_2CH_2); 2.49 (t, 2 H, SCH_2CH_2, J = 7.3 Hz); 2.50 (d, 2 H, CH_2SH, J = 8.8 Hz); 2.51 (s, 2 H, CH_2S).

3-*tert*-Butylthio-2,2-diethylpropanethiol (7) was prepared by the reaction of a 1.2 *M* Bu^{t}MgCl solution (3.3 mL, 4 mmol) with 4,4-diethyl-1,2-dithiolane (0.33 g, 2 mmol) in ether as described previously.[14] Compound **7** was obtained in a yield of 0.40 g (92%) as a colorless liquid. ^{1}H NMR, δ: 0.80 (t, 6 H, two CH_3CH_2 groups, J = 7.4 Hz); 0.90 (t, 3 H, CH_3, J = 7.3 Hz); 1.22 (t, 1 H, SH, J = 8.8 Hz); 1.32 (s, 9 H, Bu^t); 1.37 (q, 4 H, two CH_2Me groups, J = 7.4 Hz); 2.47 (s, 2 H, CH_2SBu^t); 2.50 (d, 2 H, CH_2SH, J = 8.8 Hz). Found (%): C, 59.93; H, 10.90; S, 29.24. $C_{11}H_{22}S_2$. Calculated (%): C, 60.49; H, 10.15; S, 29.36.

Reaction of 2,2-diethyl-1,3-propanedithiol 1 with 2,5-dimethyl-2,4-hexadiene (2). A solution of dithiol **1** (0.33 g, 2 mmol), diene **2** (0.22 g, 2 mmol), AIBN (16 mg, 5 mol.%), and a weighed sample of dodecane (standard for GLC) in benzene (20 mL) was refluxed for 6 h. In the course of the reaction, the composition of the reaction mixture was analyzed by GLC. After completion of the reaction, dithiolane **4**, which was identical to the obviously synthesized sample,[12] was isolated by column chromatography in a yield of 0.18 g (55%). The conversion of dithiol **1** was 85%. The conversion of diene **2** was 65%.

Reaction of 2,2-diethyl-1,3-propanedithiol 1 with decene-1. A solution of dithiol **1** (0.33 g, 2 mmol), decene-1 (0.28 g, 2 mmol), and AIBN (20 mg, 6 mol.%) in benzene (20 mL) was refluxed for 6 h. The solution was concentrated. The residue was chromatographed on a column, and 3-decylthio-2,2-diethylpropanethiol (**6**) was isolated in a yield of 0.51 g (83%) as a colorless liquid. ^{1}H NMR, δ: 0.77 (t, 6 H, two CH_3CH_2 groups, J = 7.5 Hz); 0.86 (t, 3 H, CH_3, J = 6.55 Hz); 1.19 (t, 1 H, SH, J = 8.9 Hz); 1.25 (m, 14 H, $(CH_2)_7$); 1.34 (q, 4 H, two CH_2Me groups, J = 7.5 Hz); 1.5—1.6 (m, 2 H, SCH_2CH_2); 2.48 (t, 2 H, SCH_2CH_2, J = 7.4 Hz); 2.49—2.54 (m, 4 H, CH_2SH, SCH_2C). Found (%): C, 67.4, 67.61; H, 11.75, 11.92; S, 20.61, 20.76. $C_{17}H_{36}S_2$. Calculated (%): C, 67.04; H, 11.91; S, 21.05. According to the GLC data, the yield of dithiolane **4**, which was obtained as a by-product, was 0.9 mol per mole of AIBN. The conversion of dithiol was **1** ~100%. The conversion of decene-1 was 94%.

Homolytic cyclization of 3-*tert*-butylthio-2,2-diethylpropanethiol (7). A solution of thiol **7** (0.20 g, 0.9 mmol) and AIBN (14 mg, 10 mol.%) in benzene (10 mL) was refluxed for 6 h. The solvent was concentrated. The residue was chromatographed on a column. 4,4-Diethyl-1,2-dithiolane **4** was isolated in a yield of 0.12 g (84%). Compound **4** was identical to the unambiguously synthesized sample.[12] According to the GLC data, the yield of dithione **4** formed was 90% (0.9 mol per mole of AIBN). The conversion of thiol **1** was ~98%.

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