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Abstract

Full Text

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HOMOLYTIC ISOMERIZATION OF ACETONE DI-*n*-BUTYLMERCAPTAL

In previous papers ($^{1-3}$), R. G. Petrova and we reported the first examples of radical rearrangement of mercaptals and mercaptols with migration of a phenylthio group, occurring in the liquid phase. In particular, it was shown that the diphenylmercaptols of acetone (^{2}) and acetophenone (^{3}), when heated with tert-butyl peroxide in chlorobenzene medium, undergo rearrangement with the formation of 1,2-bis(phenylthio)propane and 1,2-bis(phenylthio)ethylbenzene, respectively. In addition, in both cases formation of diphenyl disulfide and unsaturated sulfides took place—propenyl phenyl sulfide in the case of the mercaptol of acetone and α-styryl phenyl sulfide in the case of the mercaptol of acetophenone. The observed transformations may be represented by scheme 1.

$$R(CSC_6H_5)_2CH_3 \xrightarrow{[(CH_3)_3CO]_2} RCH(SC_6H_5)CH_2SC_6H_5 + (C_6H_5S)_2 + R(CSC_6H_5) = CH_2 \qquad (1)$$

(I) (II) (III)

The radical character of the rearrangement, using the example of the diphenylmercaptol of acetone, was confirmed by the fact that in the absence of peroxide the rearrangement does not occur.

The mechanism of the transformations under consideration of diphenylmercaptols, which makes it possible to explain the formation of all substances isolated from the reaction mixture (I, II, III), is represented by scheme 2.

$$R(CSC_6H_5)_2CH_3 + (CH_3)_3\dot{C}O \xrightarrow{a} R(CSC_6H_5)_2\dot{C}H_2 + (CH_3)_3COH$$

(IV)

$$\begin{aligned} R(CSC_6H_5)_2\dot{C}H_2\ (A) &\xrightarrow{b} R\dot{C}(SC_6H_5)CH_2SC_6H_5\ (B) \xrightarrow{(IV)} I + A \\ &\xrightarrow{v} R(CSC_6H_5) = CH_2 + C_6H_5\dot{S} \end{aligned} \qquad (2)$$

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$$2C_6H_5\dot{S} \xrightarrow{e} C_6H_5SSC_6H_5$$

According to this scheme, the transformation of radical A into radical B may have the character of an intramolecular rearrangement (via *b*) or proceed by the "elimination—addition" type (via *v*, *d*). We have presented evidence in favor of this transformation being realized by both pathways ([3]).

In the present work we studied the reaction of acetone di-*n*-butylmercaptal with tert-butyl peroxide, with the aim of clarifying the possibility of carrying out the rearrangement under study with migration of an alkylthio group.

It was found that acetone di-*n*-butylmercaptal isomerizes on heating with peroxide to form 1,2-di-(*n*-butylthio)propane. The radical character of this rearrangement is confirmed by the fact that isomerization does not take place in the absence of peroxide. Using the method of gas–liquid chromatography (GLC), we studied the yield of 1,2-di-(*n*-butylthio)propane as a function of the amount of tert-butyl peroxide introduced into the reaction mixture; the results obtained (14.5 moles of rearranged product per 1 mole of peroxide) testify in favor of a chain mechanism for the rearrangement being studied. In addition, in the present work, by the GLC method, the formation of trimethylcarbinol was shown, thereby confirming the initiation stage (stage *a* of scheme 2). The structure of 1,2-di-(*n*-butylthio)propane was proved by an independent synthesis

by synthesis of this compound and identification of both products by the GLC method. For comparison, 1,3-di-(*n*-butylthio)propane was also obtained.

Experimental Part

1. Isomerization of acetone di-*n*-butyl mercaptol.

a) With 40 mole % peroxide. A solution of 15 g of mercaptol in 22 ml of chlorobenzene was boiled for 10 hours, adding 4 g of tert-butyl peroxide in portions. After twofold distillation, the following were isolated:

1) 7.2 g of a fraction with b.p. 115—120° at 2 mm, from which, after distillation, 1,2-di-(*n*-butylthio)propane was obtained, b.p. 119—120° at 2 mm, n_D^{20} 1.4950, d_4^{20} 0.9279. Found MR 69.14; $C_{11}H_{24}S_2$, calculated MR 69.14. Yield 45% of theory, which corresponds to a yield of 1.2 moles of substance per 1 mole of peroxide. By the GLC method the yield of 1,2-di-(*n*-butylthio)propane was determined to be 40.6% of theory.

Found, %: C 60.36; 60.45; H 10.90; 10.90; S 28.75; 29.09
Calculated, %: C 60.00; H 10.90; S 29.10

By the GLC method it was shown that the substance obtained is identical with an authentic 1,2-di-(*n*-butylthio)propane (see Table 1).

Table 1

No.	Substance	Experiment No.	Retention time	Temperature, °C	Gas flow rate, l/hr
1	$CH_3CH(SC_4H_9)CH_2SC_4H_9$	1 (a)	6 min. 15 sec.	230	2.5
2	$CH_3CH(SC_4H_9)CH_2SC_4H_9$	authentic	6 min. 15 sec.	230	2.5
3	Mixture 1 and 2	1 (a) and authentic	6 min. 15 sec.	230	2.5
4	$C_4H_9SCH_2CH_2CH_2SC_4H_9$	4	8 min. 00 sec.	230	2.5
5	$CH_3CH(SC_4H_9)CH_2SC_4H_9$	1 (b)	7 min. 07 sec.	235	2.0
6	$CH_3CH(SC_4H_9)CH_2SC_4H_9$	authentic	7 min. 07 sec.	235	2.0
7	$C_4H_9SSC_4H_9$	1 (a)	2 min. 00 sec.	230	2.5
8	$C_4H_9SSC_4H_9$	authentic	2 min. 00 sec.	230	2.5
9	$(CH_3)_3COH$	1 (a)	3 min. 30 sec.	125	0.5
10	$(CH_3)_3COH$	authentic	3 min. 30 sec.	125	0.5

Note. Stationary phase—silicone elastomer—10—12%, carrier gas—helium, copper column 1.8 m long.

2) 3 g of a fraction with b.p. 60—110° at 2 mm, which according to GLC data contains 75% dibutyl disulfide (see Table 1).
   Yield 37% of theory.* In addition, the GLC method showed the presence of tert-butyl alcohol in the reaction mixture (see Table 1).

b) With 5 mole % peroxide. The experiment was carried out as the preceding one; 5 g of mercaptol and 0.17 g of peroxide were taken. By the GLC method the formation of 1,2-di-(*n*-butylthio)propane was determined with a yield of 75% of theory, which corresponds to a yield of 14.6 moles of substance per 1 mole of peroxide.

2. Heating of acetone di-*n*-butyl mercaptol in the absence of peroxide.

A solution of 6.4 g of mercaptol in 10 ml of chlorobenzene was boiled for 10 hours. 5.4 g of the initial mercaptol was isolated. By the GLC method the absence of 1,2-di-(*n*-butylthio)propane in the reaction mixture was established.

3. Synthesis of 1,2-di-(*n*-butylthio)propane.

From 10.1 g of 1,2-dibromopropane, 9 g of *n*-butyl mercaptan, and 2.3 g of Na in alcohol, there was obtained

* Isopropenyl *n*-butyl sulfide was not isolated in this experiment.

6 g of 1,2-dibutylthiopropane. The products of two experiments were combined and redistilled; b.p. 105° at 1 mm, n_D^{20} 1.4931, d_4^{20} 0.9265.

Found, %: C 60.13; 59.93; H 10.95; 11.07; S 29.09; 29.13
Calculated, %: C 60.00; H 10.90; S 29.10

4. **Synthesis of 1,3-di-(n-butylthio)-propane.** 1,3-Di-(n-butylthio)-propane was obtained from 7.4 g of 1,3-dichloropropane, 11.7 g of butyl mercaptan, and 3 g of sodium. Yield 65% of theory. B.p. 104° at 3 mm, n_D^{20} 1.4935, d_4^{20} 0.9291.

Found, %: C 60.12; 60.20; H 11.04; 11.15; S 28.72; 28.52
Calculated, %: C 60.00; H 10.90; S 29.10

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Note: Figure translations are in progress. See original paper for figures.

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