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Abstract

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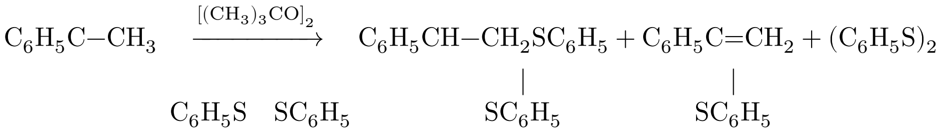
RADICAL ISOMERIZATION OF ACETOPHENONE DIPHENYLMERCAPTOL

In a previous article (¹) we described the radical rearrangement of acetone diphenylmercaptol into 1,2-bis(phenylthio)propane under the action of tert-butyl peroxide on heating in chlorobenzene; in addition, diphenyl disulfide and phenyl isopropenyl sulfide were formed. The radical character of the rearrangement was confirmed by the absence of isomerization when acetone diphenylmercaptol was heated without peroxide.

In order to elucidate the influence of the structure of the mercaptol on the rearrangement, in the present work we have studied the isomerization of acetophenone diphenylmercaptol under the action of tert-butyl peroxide. In this case, formation of 1,2-bis(phenylthio)ethylbenzene, diphenyl disulfide, and α-phenylthio styrene also took place.



$$\underset{C_6H_5S\quad SC_6H_5}{C_6H_5C{-}CH_3} \xrightarrow{[(CH_3)_3CO]_2} C_6H_5\underset{\substack{|\\ SC_6H_5}}{CH}{-}CH_2SC_6H_5 + C_6H_5\underset{\substack{|\\ SC_6H_5}}{C}{=}CH_2 + (C_6H_5S)_2$$

Among the reaction products, diphenylmercaptol of phenylacetic aldehyde was not found; its formation might have been expected if the migrating group had been phenyl.

It turned out that acetophenone diphenylmercaptol, in contrast to acetone diphenylmercaptol, is partially isomerized on heating in the absence of peroxide. We assumed that acetophenone diphenylmercaptol dissociates on heating into radicals capable of initiating isomerization. To confirm this assumption, an attempt was made to initiate the isomerization of acetone diphenylmercaptol by adding acetophenone diphenylmercaptol (instead of tert-butyl peroxide), and a positive result was obtained.

Assuming that the rearrangement under study has a chain character, the following scheme may be proposed to describe this rearrangement:

$$
\begin{aligned}
1.\quad & [(CH_3)_3CO]_2 \overset{a}{\rightarrow} (CH_3)_3CO^{\bullet}\ (X^{\bullet}) \\
& RC(SC_6H_5)_2CH_3 + X^{\bullet} \overset{b}{\rightarrow} \underset{A}{RC(SC_6H_5)_2\dot{C}H_2} + HX \\
& RC(SC_6H_5)_2CH_2^{\bullet} \begin{cases} \overset{v}{\rightarrow} \underset{B}{R\dot{C}(SC_6H_5)CH_2SC_6H_5} \\ \overset{g}{\rightarrow} RC(SC_6H_5){=}CH_2 + R\dot{S} \end{cases} \\
& 2R\dot{S} \overset{d}{\rightarrow} RS{-}SR
\end{aligned}
$$

An essential feature of this scheme is the transformation of radical A into radical B (stage *v*).

This transformation may be intramolecular in character (1,2-migration of the arylthio group) or may proceed by an intermolecular mechanism of the elimination–addition type (see scheme 2).

$$
2.\quad \underset{A}{RC(SC_6H_5)_2CH_2^{\bullet}} \xrightarrow[\text{v}]{\text{isomerization}} \underset{B}{\dot{R}C(SC_6H_5)CH_2SC_6H_5}
$$

$$
\searrow\ \text{v}'\ RC(SC_6H_5){=}CH_2 + C_6H_5\dot{S}\ \nearrow\ \text{v}''
$$

To check the possibility that the rearrangement under study proceeds by an intermolecular type, we investigated the rearrangement of acetophenone diphenylmercaptol in the presence of phenylisopropenyl sulfide.

Indeed, in this case a small amount (about 4% of theory) of 1,2-bis(phenylthio)propane was obtained, which indicates the addition of phenylthio groups, formed in the process in scheme 2, to the phenylisopropenyl sulfide taken. However, the low yield of 1,2-bis(phenylthio)propane makes the intramolecular isomerization of radical A into radical B probable. The structure of the starting acetophenone diphenylmercaptol was confirmed by its hydrolysis to acetophenone and by study of the IR spectra, which showed the presence of frequencies characteristic of the methyl group.

The structure of 1,2-bis(phenylthio)ethylbenzene was confirmed by its inability to undergo hydrolysis and by IR spectra showing the absence of frequencies characteristic of the methyl group*. The structure of phenyl-α-styryl sulfide was proved by hydrolysis to acetophenone.

The synthesis and structure of 1,2-bis(phenylthio)propane and phenylisopropenyl sulfide were described in the preceding paper (1).

Experimental Part

1. Preparation of acetophenone diphenylmercaptol. A mixture of 11 g of acetophenone and 22 g of thiophenol was treated with hydrogen chloride at 50° for 3 hours. After 12 hours the crystals that separated were isolated and washed with hexane. The filtrate was washed with water, dried over $CaCl_2$, and evaporated. In all, 27.8 g of crystalline acetophenone diphenylmercaptol was obtained, m.p. 55° (from heptane). Yield 94% of theory. Literature data: m.p. 54.5-55° (from ethyl alcohol) (2).

Found, %: C 74.23; 74.41; H 5.47; 5.55
$C_{20}H_{18}S_2$. Calculated, %: C 74.52; H 5.59

Investigation of the substance by IR spectroscopy showed the presence in the spectrum of frequencies characteristic of the methyl group (1378 cm^{-1}, 1450 cm^{-1}).

On hydrolysis of the substance with an alcoholic solution of sulema, followed by treatment with 2,4-dinitrophenylhydrazine, acetophenone 2,4-dinitrophenylhydrazone was obtained, identified with an authentic sample by the absence of depression of the melting point of the mixed sample.

II. Isomerization of acetophenone diphenylmercaptol.

a) In the presence of peroxide. A solution of 15 g of the mercaptol and 2.7 g of tert-butyl peroxide in 22 ml of chlorobenzene was boiled for 10 hours. From the reaction mixture the following products were obtained by fractionation:

1) 7.5 g of a fraction with b.p. 120–140° at 1 mm, consisting mainly of α-phenylthiostyrene with a small impurity of diphenyl disulfide. On hydrolysis of this mixture with an alcoholic solution of sulema and treatment of the hydrolysate with 2,4-dinitrophenylhydrazine, acetophenone 2,4-dinitrophenylhydrazone was obtained in good yield, identified with an authentic sample by the absence of depression of the melting point of the mixed sample.
2) 3 g of diphenyl disulfide (yield about 65% of theory), identified with an authentic sample by the absence of depression of the melting point of the mixed sample.
3) 3.6 g of 1,2-bis(phenylthio)ethylbenzene with b.p. 210–213° at 1 mm, m.p. 57.5° (from hexane). Yield 24% of theory.

Found, %: C 74.56; 74.79; H 5.60; 5.56
$C_{20}H_{18}S_2$. Calculated, %: C 74.52; H 5.59

* The IR spectra were recorded in the optical laboratory of the Institute of Organoelement Compounds, Academy of Sciences of the USSR, by N. A. Chumaevskii, to whom the authors express their gratitude.

Literature data: m.p. 57-58° (^{3}). The substance is not hydrolyzed on heating with an alcoholic solution of sublimate. A mixed-melting-point test with the starting acetophenone diphenylmercaptol shows a depression of the melting point. The IR spectrum of the substance contains no frequencies characteristic of a methyl group.

b) **Without peroxide.** A solution of 10 g of the mercaptol in 15 ml of chlorobenzene was boiled for 10 h. After removal of the solvent, the residue was fractionated. From the fraction with b.p. 210-215° at 2 mm, a crystalline substance with m.p. 56° (from hexane) was isolated, identical with the 1,2-bis(phenylthio)ethylbenzene obtained earlier. Yield 35% (of theory).

III. **Isomerization of acetophenone diphenylmercaptol in the presence of acetophenone diphenylmercaptol.** To a solution of 1 g of acetophenone diphenylmercaptol in 1.5 ml of chlorobenzene, 0.5 g of acetophenone diphenylmercaptol was added in three portions. After 10 hours of boiling, the reaction mixture was examined by gas-liquid chromatography. The presence of 1,2-diphenylthiopropane in the mixture was shown (see Table 1).

Table 1

Gas-liquid chromatography data*

Substance	Experiment No.	Temp., °C	Gas flow rate, l/h	Retention time
1. a) $CH_3-CH(SC_6H_5)-CH_2SC_6H_5$	IV	230	4	26 min. 00 sec.
b) $CH_3-CH(SC_6H_5)-CH_2SC_6H_5$	known sample	230	4	25 min. 30 sec.
2. a) $CH_3-CH(SC_6H_5)-CH_2SC_6H_5$	III	233	2	28 min. 12 sec.
b) $CH_3-CH(SC_6H_5)-CH_2SC_6H_5$	known sample	233	2	28 min. 30 sec.

* Chromatography was carried out on a glass column 2 m long; stationary phase —silicone elastomer, 10%; carrier gas—helium.

IV. **Reaction of acetophenone diphenylmercaptol with phenylisopropenyl sulfide.** A mixture of 2.3 g of the mercaptol, 1.1 g of phenylisopropenyl sulfide, and 0.5 g of tert-butyl peroxide in a solution of 4 ml of chlorobenzene was boiled for 10 h. By gas-liquid chromatography it was shown that the reaction mixture contained 1,2-diphenylthiopropane (see Table 1), the yield of which is approximately 4% of theory.

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