# HOMOLYTIC REARRANGEMENT WITH THE MIGRATION

# OF AN ALKYLTHIO OR ARYLTHIO GROUP\*

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In previous papers [1-4] in collaboration with Freidlina we have described a free-radical rearrangement in which the migration of alkylthio or arylthio groups occurs. Thus, 2,2-bisphenylthiopropane [2] is isomerized into 1,2-bisphenylthiopropane when heated in chlorobenzene in presence of t-butyl peroxide; in addition, diphenyl disulfide and isopropenyl phenyl sulfide are formed. The free radical character of the rearrangement was confirmed by the absence of isomerization when the mercaptole was heated in absence of the peroxide. We later found analogous rearrangements for (1,1-bisphenylthioethyl)benzene [3] and 2,2-bisbutylthiopropane [4].

$$\operatorname{RC}(\operatorname{SR}')_{2}\operatorname{CH}_{3} \longrightarrow \operatorname{RCH}(\operatorname{SR}') \operatorname{CH}_{2}\operatorname{SR}'$$

$$\operatorname{RC}(\operatorname{SR}')_{2} \operatorname{CH}_{3} \longrightarrow \operatorname{RC}(\operatorname{SR}') = \operatorname{CH}_{2} + (\operatorname{R}'S)_{2}$$
(1)

We have proposed [2-4] the following scheme to describe the mechanism of the rearrangement:

(A) 
$$RC(SR')_2CH_3 \xrightarrow{(CH_3)_3C\dot{O}} (CH_3)_3COH$$
  
a)  $\begin{bmatrix} (CH_3)_3CO \end{bmatrix}_2$   
(B)  $RC(SR')_2\dot{C}H_2$   
(B)  $R\dot{C}(SR')CH_2SR' \xrightarrow{C} RC(SR')=CH_2 + R'\dot{S}$   
d)  $+A$   
 $RCH(SR')CH_2SR' + B$   $2R'\dot{S} \xrightarrow{A} R'SSR'$ 
(2)

For the case of 2,2-bisbutylthiopropane [4] it was found that even 5 moles percent of t-butyl peroxide is sufficient for the rearrangement product to be formed in 75% yield, which indicates that the process has a chain mechanism. The isomerization of the radical B into the radical C (scheme 2) may have an intramolecular character [1,2-migration of the alkyl or aryl)thio group-stage (b) in scheme 2] or may be intermolecular [elimination-addition reactions-stage (c)-(f) in scheme 2].

Τ	ABL	Ε1.	RC(SR	$)_2CH_3$
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R	СН <sup>*</sup>	C <sub>6</sub> H <sup>*</sup>	COOC₂H₅	CF,	СН3	СН	CH <sub>3</sub>
R'	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	$C_6H_5$	C <sub>6</sub> H₄C <b>H</b> <sub>3</sub> - <i>p</i>	C <sub>6</sub> H₄NO₂- <i>p</i>	C4H9

• These cases are described in [2-4].

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TABLE 2

Mercaptole	Conver- sion, %	Rearrange- ment, %on mercaptole that reacted
$\begin{array}{c} {\rm CH_{3}C} \; ({\rm SC_{6}H_{5}})_{2} \; {\rm CF_{3}} \\ {\rm CH_{3}C} \; ({\rm SC_{6}H_{5}})_{2} \; {\rm COOC_{2}H_{5}} \\ {\rm CH_{3}C} \; ({\rm SC_{6}H_{5}})_{2} \; {\rm CH_{3}} \\ {\rm CH_{3}C} \; ({\rm SC_{6}H_{5}})_{2} \; {\rm CH_{3}} \\ {\rm CH_{3}C} \; ({\rm SC_{6}H_{5}})_{2} \; {\rm C_{6}H_{5}} \end{array}$	0 21 62 100	0 30 24

To check on the possibility of the rearrangement occurring by an intermolecular mechanism we studied the rearrangement of (1,1-bisphenylthioethyl)benzene in presence of isopropenyl phenyl sulfide [3]. We then obtained a small amount (about 45%yield) of 1,2-bisphenylthiopropane, which is evidence of the addition of phenylthio groups to the isopropenyl phenyl sulfide taken [stage (f) in scheme 2]. However, the lowness of the yield of 1,2bisphenylthiopropane makes it probable that intramolecular isomerization plays some part [stage (b) in scheme 2]. In a number of cases we showed by gas-liquid chromatography that the reaction mixture contained t-butyl alcohol, which confirmed the oc-

currence of the initiation stage in our proposed scheme for the rearrangement [stages (a) and (a') in scheme 2].

Mercaptole	Rearrange- ment, % on mercaptole that reacted	Conver- sion, %	Molar ratio re- arranged: un- saturated product
$(CH_3)_2C(SC_6H_4NO_{2^-}p)_2$ $(CH_3)_2C(SC_6H_5)_2$ $(CH_3)_2C(SC_6H_5)_2$ $(CH_3)_2C(SC_6H_4CH_{3^-}p)_2$ $(CH_3)_2C(SC_4H_9)_2$	$     \begin{array}{c}       0 \\       30 \\       40 \\       50     \end{array} $	$     \begin{array}{c}       0 \\       62 \\       39 \\       90     \end{array} $	0,4 0,7 1,2

TABLE 3

To determine the effect of the structure of the mercaptole on the rearrangement, in the present investigation we studied a series of mercaptoles containing different groups, both in the  $\alpha$ -position to the mercaptole grouping and in the migrating R,S group; the mercaptoles studied are listed in Table 1.

With all the mercaptoles the experiments were carried out under the same conditions. Heating of ethyl 2,2bisphenylthiopropionate with t-butyl peroxide led only to partial decomposition with elimination of  $C_6H_5S$  groups and formation of diphenyl disulfide. 1,1,1-Trifluoro-2,2-bisphenylthiopropane was recovered unchanged from the reaction. The results on the effect of varying the group R are summarized in Table 2.

It will be seen that with increase in the electronegativity of R in the mercaptole  $RC(SR')_2CH_3$  the degree of conversion falls sharply. On the other hand, we studied the effect of the nature of the group (R') in the migrating group. It was shown that 2,2-bis-p-tolythiopropane isomerizes like 2,2-bisphenylthiopropane. The structure of the 1,2-bis-p-tolythiopropane obtained was proved by an independent synthesis

 $CH_{3}CHBr CH_{2}Br \xrightarrow{p-CH_{3}C_{4}H_{4}SN_{4}} \rightarrow CH_{3}CH (SC_{6}H_{4}CH_{3})CH_{2}SC_{6} H_{4}CH_{3} \cdot$ 

The structure of the isopropenyl p-tolyl sulfide obtained in this process was confirmed by its hydrolysis to acetone. When the reaction was carried out in absence of the peroxide we isolated the original mercaptole. The effect of an electron-accepting substituent in the migrating group was studied for the case of 2,2-bis(p-nitrophenylthio)propane. Under the conditions studied this mercaptole does not change when heated in presence of the peroxide. The results are summarized in Table 3.

The results show that the nature of the group in the migrating group has an appreciable effect of the yield of the rearranged product and particularly on the ratio of the yields of the products of the competing reactions [routes (a) and (b) in scheme 1].

### EXPERIMENTAL

Heating of Ethyl 2,2-Bisphenylthiopropionate in Presence of t-Butyl Peroxide. The original mercaptole was prepared in the usual way from ethyl pyruvate and benzenethiol; b.p. 200° (2 mm);  $n_D^{20}$  1.6003;  $d_4^{20}$  1.1713. Found: C 64.08; 64.06; H 5.83; 5.82; S 20.21; 20.22%; MR 92.91. Calculated: C 64.15; H 5.66; S 20.10%; MR 91.96. Hydrolysis of the ester gave 2,2-bisphenylthiopropionic acid, m.p. 114-115° (from petroleum ether). The literature [5] gives m.p. 116-117°. Found: C 62.38; 62.24; H 5.16; 5.13; 22.34%.  $C_{15}H_{14}O_2S_2$ . Calculated: C 62.10; H 4.83; S 22.10%.

A solution of 10 g of ethyl 2,2-bisphenylthiopropionate in 15 ml of chlorobenzene was boiled for ten hours with the addition of 1.8 g (40 moles percent) of t-butyl peroxide in portions. Solvent was driven off, and the residue was

fractionated, after which each fraction was redistilled. We isolated: a) 0.8 g of diphenyl disulfide, m.p. 58-59°, identified with a known sample; b) 6 g of the original mercaptole; b.p. 197° (1 mm);  $n_D^{20}$  1.6010;  $d_4^{20}$  1.1736; c) 0.5 g of a higher-boiling residue, which corresponded in analysis to the original mercaptole. This residue did not contain rearranged product, for on hydrolysis it gave an acid of m.p. 114-115° (from hexane). A mixture with the acid obtained by the hydrolysis of the original mercaptole melted without depression. In this experiment no unsaturated sulfide was isolated.

Heating of 1,1,1-Trifluoro-2,2-bisphenylthiopropane in Presence of t-Butyl Peroxide. The original mercaptole was prepared from 1,1,1-trifluoroacetone and benzenethiol in presence of anhydrous ZnCl<sub>2</sub> and dry HCl at 10-12°; b.p. 154° (2 mm);  $n_D^{20}$  1.5725;  $d_4^{20}$  1.2699; found: F 18.05; 18.15%; MR 81.42.  $C_{15}H_{13}F_3S_26J$ . Calculated: F18.15%; MR 80.75. This mercaptole was hydrolyzed by mercuric chloride solution only when heated with it in a sealed tube at 140-145°. The infrared spectrum of the mercaptole contained frequencies characteristic for the methyl group. The experimental procedure was similar to that of the preceding experiment. From 9 g of the mercaptole, 8 g was recovered unchanged ( $n_D^{20}$  1.5755), after distillation; it was identified with a known sample by gas-liquid chromatrography.

Isomerization of 2,2-Bis-p-tolylthiopropane. The procedure was as in the first experiment. From 13 g of the mercaptole we obtained, after removal of solvent: a) 2.6 g (15%) of 1,2-bis-p-tolylpropane, which after redistillation had b.p. 205° (2 mm);  $n_D^{20}$  1.6065;  $d_4^{20}$  1.0886. Found: C 70.78; 70.87; H 7.08; 7.06%; MR 91.00.  $C_{17}H_{20}S_26^{d}$ . Calculated: C 70.83; H 6.95%; MR 90.30.

Disulfone, m.p. 135-136° (from alcohol). Found: C 58.14; 58.00; H 5.96; 5.78; S 18.26; 18.22%. Calculated: C 57.98; H 5.68; S 18.18%. A mixture with known 1,2-bis-p-tolylsulfonylpropane melted without depression.

b) 1.8 g (24%) of a fraction consisting in the main of isopropenyl p-tolyl sulfide; b.p. 80° (2 mm);  $n_D^{20}$  1.5550;  $d_4^{20}$  0.9921. Found: C 72.13; 72.31; H 7.68; 7.74%; MR 53.06.  $C_{10}H_{12}S4 \pm$ . Calculated: C 73.15; H 7.31%; MR 52.71. Hydrolysis of the substance with an alcoholic solution of mercuric chloride gave acetone, identified as its 2,4-dinitrophenylhydrazone.

c) 5 g of an intermediate fraction, from which some of the original mercaptole was isolated (the fraction was not investigated more closely).

Heating of 2,2-Bis-p-tolythiopropane in Absence of the Peroxide. A solution of 3.2 g of the mercaptole in 4.5 ml of chlorobenzene was boiled for ten hours. Solvent was driven off, and we isolated 3 g of a crystalline substance, m.p. 63-64°. A mixture of this with the original mercaptole melted without depression.

Synthesis of 1,2-Bis-p-tolylthiopropane. From 8.2 g of 1,2-dibromopropane, 10 g of p-toluenethiol, and 1.85 g of sodium in alcohol we obtained 6.1 g of 1,2-bis-p-tolythiopropane; b.p. 214-216° (3 mm);  $n_D^{20}$  1.6075;  $d_4^{20}$  1.0930. Found: C 70.59; 70.44; H 6.74; 6.71% MR 91.05.  $C_{17}H_{20}S_26 =$ . Calculated: C 70.83; H 6.95%; MR 90.30. Disulfone, m.p. 136-137° (from alcohol).

Heating of 2,2-Bis(p-nitrophenylthio)propane in Presence of t-Butyl Peroxide. The experiment was carried out under the above-described conditions. From 12.5 g of the mercaptole we isolated, after the removal of solvent, 12.2 g of a crystalline substance, which after recrystallization melted without depression in admixture with some of the original mercaptole.

### SUMMARY

1. We have studied new cases of the homolytic rearrangement of mercaptoles that we described previously; the object was to establish the effect of the structure of the mercaptole on the rearrangement.

2. When heated with t-butyl peroxide, 2,2-bis-p-tolylthiopropane, like the previously studied 2,2-bisbutylthiopropane, 2,2-bisphenylthiopropane, and (1,1-bisphenylthioethyl)benzene, undergoes rearrangement with formation of 1,2-bis-p-tolylthiopropane. Under the same conditions 2,2-bis(p-nitrophenylthio)propane and 1,1,1-trifluoro-2,2-bisphenylthiopropane remain unchanged.

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