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A. B. TERENT'EV, Corresponding Member of the Academy of Sciences of the USSR, R. Kh. FREIDLINA

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Abstract

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A. B. TERENT' EV, Corresponding Member of the Academy of Sciences of the USSR, R. Kh. FREIDLINA

REARRANGEMENT OF α,α-BIS-(n-BUTYLTHIO)ETHYLBENZE INTO α,β-BIS-(n-BUTYLTHIO)ETHYLBENZENE UNDER THE ACTION OF tert-BUTYL PEROXIDE

We, together with R. G. Petrova ($^{1-4}$), have shown that dialkyl and diaryl mercaptals of acetone, when heated in chlorobenzene with tert-butyl peroxide, undergo isomerization with the formation of 1,2-bisalkyl-(aryl)-thiopropanes. At the same time, the corresponding dialkyl-diaryl disulfides and 2-alkyl-(aryl)-thiopropenes are formed according to the scheme:

$$CH_3C(SR)_2CH_3 \xrightarrow[130^\circ\text{–}135^\circ]{((CH_3)_3CO)_2} \begin{cases} CH_3CH(SR)CH_2SR \\ RS{-}SR + CH_3C(SR){=}CH_2 \end{cases}$$

where R = n-C_4H_9, C_6H_5, $CH_3C_6H_4$. In the absence of peroxide these transformations do not occur.

Using acetone di-n-butyl mercaptal as an example, it was shown that this rearrangement has an intramolecular, chain, radical character (^{2}). For the reactions studied, the following scheme was proposed:

$$((CH_3)_3CO)_2 \to (CH_3)_3C\dot{O}$$

$$(CH_3)_3C\dot{O} + CH_3C(SR)_2CH_3 \to (CH_3)_3COH + CH_3C(SR)_2\dot{C}H_2 \quad (A)$$

$$CH_3C(SR)_2\dot{C}H_2 \xrightarrow{\text{rearrangement}} CH_3\dot{C}(SR)CH_2SR$$

$$CH_3C(SR)_2\dot{C}H_2 \to CH_3C(SR){=}CH_2 + \dot{S}R$$

$$2R\dot{S} \rightarrow RS{-}SR$$

$$CH_3\dot{C}(SR)CH_2SR + CH_3C(SR)_2CH_2 \rightarrow CH_3CH(SR)CH_2SR + A \quad \text{(chain)}$$

It turned out that acetophenone diphenyl mercaptal undergoes the same transformations upon heating in chlorobenzene both in the presence of peroxide and in its absence (^{3}). The mechanism of this reaction is not entirely clear, although there are some data in favor of the supposition that these transformations also have a radical character (^{3}).

In the present work we studied the behavior of acetophenone di-*n*-butyl mercaptal upon heating in chlorobenzene both in the presence and in the absence of peroxide; the results obtained are summarized in Table 1.

As is seen from the data of Table 1, in the absence of peroxide (experiment 8) α, β-bis-(*n*-butylthio)ethylbenzene is not formed; in the presence of peroxide the yield of this product (in experiment 6) amounted to 15.3 moles per mole of peroxide, while the concentration of the solution (experiments 5 and 7) has no substantial effect on the yield of the rearranged product.

All these data characterize the reaction studied as having a radical, chain, and, apparently, intramolecular character. It was natural to propose that this transformation may be described by a scheme analogous to that adopted for the isomerization of acetone dialkyl mercaptals:

$$(CH_3)_3C\dot{O} + C_6H_5C(SC_4H_9)_2CH_3 \xrightarrow{a} (CH_3)_3COH + C_6H_5C(SC_4H_9)_2\dot{C}H_2 \quad (A)$$

$$C_6H_5C(SC_4H_9)_2\dot{C}H_2 \xrightarrow[\text{isomeriz.}]{\text{b}} C_6H_5\dot{C}(SC_4H_9)CH_2SC_4H_9 \quad (B)$$

$$C_6H_5C(SC_4H_9)_2\dot{C}H_2 \xrightarrow{\text{v}} C_6H_5C(SC_4H_9){=}CH_2 + C_4H_9\dot{S}$$

$$2\,C_4H_9\dot{S} \xrightarrow{\text{g}} C_4H_9S{-}SC_4H_9$$

$$C_6H_5\dot{C}(SC_4H_9)CH_2SC_4H_9 + C_6H_5C(SC_4H_9)_2CH_3 \xrightarrow{\text{d}}$$

$$\rightarrow C_6H_5CH(SC_4H_9)CH_2SC_4H_9 + A \quad \text{(chain)}$$

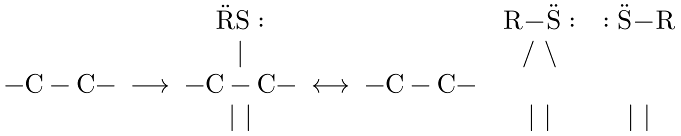
Here, however, we encounter the following difficulty: according to this scheme, as a result of the rearrangement (stage b), relatively stable benzyl radicals B are formed which, by abstracting a hydrogen atom from a mercaptan molecule, continue the chain. Meanwhile, the literature contains a number of indications ($^{5-8}$) that benzyl radicals in the liquid phase are not capable of abstracting hydrogen atoms and thus of transferring the chain. Recently, however, works have appeared showing that benzyl radicals are, to a certain extent, capable of abstracting hydrogen atoms from isopropylbenzene (^{9}) and *n*-chlorotoluene (^{10}). In the latter work the activation energy was estimated for the reaction

$$C_6H_5\dot{C}H_2 + \text{n-}CH_3C_6H_4Cl \rightarrow C_6H_5CH_3 + \dot{C}H_2C_6H_4Cl,$$

and was found to be 20.3 kcal/mol.

Such a high activation energy indicates that reactions of this kind can be significant only at a sufficiently high temperature.

In light of the above, it should be assumed that, if the scheme of radical isomerization of acetophenone dibutyl mercaptal given above is correct, then abstraction of a hydrogen atom from the methyl group adjacent to the $C_6H_5C(SC_4H_9)_2$ grouping proceeds comparatively easily, and the radicals formed, $C_6H_5C(SC_4H_9)_2\dot{C}H_2$, are more stable than primary hydrocarbon radicals. Possibly, a more correct assumption here is that this rearrangement proceeds through bridged structures of the type



$$-\mathrm{C}-\mathrm{C}- \longrightarrow \underset{|\ |}{\overset{\overset{\ddot{\mathrm{R}}\mathrm{S}:}{|}}{-\mathrm{C}-\mathrm{C}-}} \longleftrightarrow -\mathrm{C}-\mathrm{C}- \quad \underset{|\ |}{\overset{\mathrm{R}-\ddot{\mathrm{S}}:}{/\ \backslash}} \quad \underset{|\ |}{:\ddot{\mathrm{S}}-\mathrm{R}}$$

especially since there are data for the sulfur atom indicating the possibility of expansion of its electron shell in radical reactions (^{12}).

Experimental Part

1. α,α-**Bis-(*n*-butylthio)-ethylbenzene** was obtained by the usual method from acetophenone and butyl mercaptan in the presence of hydrogen chloride at 50°. B.p. 168–169° at 3 mm, n_D^{20} 1.5465; d_4^{20} 1.0024. *MR* found 89.15. $C_{16}H_{26}S_2^3$ [[unclear: symbol after formula]]. *MR* calculated 89.28.

$$\begin{aligned} \text{Found }\%&:\ \text{C } 68.16,\ 68.15;\quad \text{H } 9.23,\ 9.04 \\ \text{Calculated }\%&:\ \text{C } 68.09;\quad \text{H } 9.22 \end{aligned}$$

Yield 30% of theory.

2. **Isomerization of α,α-bis-(n-butylthio)-ethylbenzene in the presence of tert-butyl peroxide.** A solution of 10 g of α,α-bis-(n-butylthio)-ethylbenzene in 15 ml of chlorobenzene was boiled for 10 h, adding 2 g of tert-butyl peroxide in portions. After removal of the solvent, the residue was fractionated. The following fractions were obtained:

1) 60–100° at 1 mm, weight 3.7 g, which, as shown by gas-liquid chromatography, contains dibutyl disulfide and, apparently, an unidentified sulfide –α-butylthiostyrene.

2) 140–180° at 1 mm, weight 4.4 g, from which, on redistillation, α,β-bis-(n-butylthio)-ethylbenzene was obtained, b.p. 185° at 3 mm, n_D^{20} 1.5530; d_4^{20} 1.0067. MR found 89.63. $C_{16}H_{26}S_2^3$ [[unclear: symbol after formula]], calculated 89.28. Yield 40% of theory. By gas-liquid chromatography the product was identified with an authentic α,β-bis-(n-butylthio)-ethylbenzene sample. On oxidation with hydrogen peroxide in acetic acid, a sulfone with m.p. 93° (from alcohol) was obtained. Yield 65%.

Found %: C 55.28, 55.32; H 7.18, 7.35
$C_{16}H_{26}S_2O_4$. Calculated %: C 55.55; H 7.52

A mixed sample with an authentic α,β-bis-(n-butylsulfonyl)-ethylbenzene gave no depression of the melting point.

3. **Heating of α,α-bis-(n-butylthio)-ethylbenzene in the absence of peroxide.** The experiment was carried out analogously to the preceding one, but without tert-butyl peroxide.

On fractionation the following was obtained:

1) 3 g of a fraction boiling up to 100° at 1 mm, n_D^{20} 1.5422; consists mainly of α-butylthiostyrene; b.p. 107—108° at 1 mm, n_D^{20} 1.5450; d_4^{20} 0.9849. MR found 61.60, $C_{12}H_{16}S_4F$, calculated 61.95.

Table 1*

Effect of the amount of tert-butyl peroxide and of the mercaptan concentration on the yield of the rearranged product

	Experiment no.	Experiment no.	Experiment no.	Experiment no.
	5	6	7	8
Amount of peroxide, mol. % relative to mercaptan	40	5	40	0

	Experiment no.	Experiment no.	Experiment no.	Experiment no.
Concentration of mercaptan solution in chlorobenzene, %	35	35	6	35
Yield of α,β-bis-(n-butylthio)-ethylbenzene, % of theory	45.6	76.4	36	0
Yield of α,β-dibutylthio derivative, in moles per mole of peroxide	1.15	15.3	0.9	–

* Analysis was carried out by the GLC method with calibration against a standard. Charges: experiments 5, 7, 8—2 g; experiment 6—4 g. Heating time—10 h.

On hydrolysis of the substance with a solution of sublimate, acetophenone was obtained, identified as the 2,4-dinitrophenylhydrazone. A mixed sample with an authentic 2,4-dinitrophenylhydrazone of acetophenone gave no depression of the melting point. In addition, the presence of di-*n*-butyl disulfide in this fraction was shown by gas-liquid chromatography.

2) 5.9 g of the starting α,α-bis-(n-butylthio)-ethylbenzene.

On hydrolysis with a solution of sublimate, acetophenone was obtained in quantitative yield and identified as the 2,4-dinitrophenylhydrazone. A mixed sample with an authentic 2,4-dinitrophenylhydrazone of acetophenone gave no depression of the melting point.

By gas-liquid chromatography it was shown that α,β-bis-(n-butylthio)-ethylbenzene was absent from the reaction mixture.

4. **Preparation of α,β-bis-(n-butylthio)-ethylbenzene** was carried out by the known procedure by addition of di-*n*-butyl disulfide to styrene in the presence of iodine. B.p. 170°/2 mm, n_D^{20} 1.5395; d_4^{20} 1.0010. Yield 50% of theory. *MR* found 88.4; calculated 89.28.

Found, %: C 67.70, 67.88; H 8.74, 8.60
Calculated, %: C 68.09; H 9.22

Sulfone. M.p. 92–93° (from alcohol). Yield 80% of theory.

Institute of Organoelement Compounds
Academy of Sciences of the USSR

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

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