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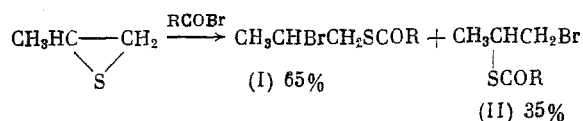9. L. V. Nesterov and N. A. Aleksandrova, Izv. Akad. Nauk SSSR, Ser. Khim., 971 (1978).

ISOMERIZATION OF THIOCARBOXYLIC ESTERS OF 1-BROMO-2-PROPANOL

AND 2-BROMO-1-PROPANOL

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In previous work [1-3], we discovered the isomerization of various esters of 1-bromo-2-propanol and 2-bromo-1-propanol and proposed a mechanism for this process, entailing the formation of a five-membered acyloxonium intermediate or transition state.

It was of interest to study the isomerization of the sulfur analogs of these bromopropanol esters. Esters of bromopropanols and thioacetic or thiobenzoic acid were selected as the model compounds. These esters were prepared according to reported procedures [4, 5] by the reaction of propylene sulfide with acetyl bromide or benzoyl bromide.

$$CH_3HC \overset{\displaystyle\diagdown}{\underset{\displaystyle S}{\diagup}} CH_2 \xrightarrow{\text{RCOBr}} CH_3CHBrCH_2SCOR + \underset{\substack{|\\ SCOR \\ \text{(II) } 35\%}}{CH_3CHCH_2Br}$$

(I) 65%

$R = CH_3,\ C_6H_5.$

The (I)/(II) product ratio was 2:1 in contrast to the data of Schwartz [5], indicating that the corresponding primary bromide is the major product.

The isomerization of the thiocarboxylic esters of 1-bromo-2-propanol and 2-bromo-1-propanol was studied at 100°C in CCl_4, octane, benzene, toluene, methylene chloride, and nitrobenzene, as well as without solvent. The reaction course was followed by NMR spectroscopy. The corresponding primary bromide was the major product in the reaction mixture after the establishment of equilibrium [5].

$$CH_3CHBrCH_2SCOR \rightleftarrows \underset{\substack{|\\ SCOR \\ \text{(II) } 85\%}}{CH_3CHCH_2Br}$$

(I) 15%
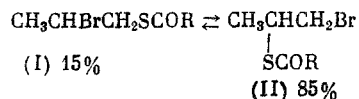
The equilibrium mixture in all cases contained 15% (I) and 85% (II).

The rate of the isomerization, which is an equilibrium type reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$,

TABLE 1. Isomerization Rate Constants (sec^{-1}) of Thioacetates and Thiobenzoates of 1-Bromo-2-propanol and 2-Bromo-1-propanol*

Compound	$C_6H_5NO_2$	CD_2Cl_2	Without solvent
(I, R=Me)	$1.4 \cdot 10^{-6}$	$6.8 \cdot 10^{-7}$	$2.7 \cdot 10^{-7}$
(I, R=Ph)	$1.4 \cdot 10^{-6}$	$8.0 \cdot 10^{-7}$	$3.1 \cdot 10^{-7}$
(II, R=Me)	$1.6 \cdot 10^{-6}$	$7.3 \cdot 10^{-7}$	$3.3 \cdot 10^{-7}$
(II, R=Ph)	$1.3 \cdot 10^{-6}$	$8.2 \cdot 10^{-7}$	$3.8 \cdot 10^{-7}$

*Decomposition of the reaction mixture occurs under these conditions in benzene, toluene, octane, and carbon tetrachloride.

was evaluated relative to the isomerization constant, which is the sum of the rate constants of the forward and reverse reactions and is calculated using the following equation

$$k_{\text{is}} = \frac{1}{t} \ln \frac{[\text{B}]_{\text{eq}}}{[\text{B}]_{\text{eq}} - x}$$

where $[\text{B}]_{\text{eq}}$ is the equilibrium concentration of $\text{B}^{\dagger}$ and x is the decrease in the concentration of A up to time t.

Table 1 gives the results for the isomerization of the thioacetates and thiobenzoates of 1-bromo-2-propanol and 2-bromo-1-propanol, which show that the isomerization rate of the thiocarboxylic esters of these bromopropanols depends on solvent polarity. Thus, the amount of the second isomer is significantly higher after heating in nitrobenzene at 100°C for 5 h, while maintaining the starting compounds in CCl_4, toluene, benzene, and octane at 100°C for even 300 h does not lead to the isomerization of (I) and (II), but rather to their gradual decomposition. Heating the thioacetates and thiobenzoates of these bromopropanols without solvent leads to their isomerization with k_{is} values comparable to those in CD_2Cl_2.

We should note that k_{is} is independent of the nature of the R group in the thiocarboxylic groups, i.e., k_{is} for the thioacetates is approximately equal to k_{is} for the thiobenzoates. However, in the case of isomerization of bromopropanol esters not containing sulfur, going from acetates to benzoates leads to a more than 10-fold increase in k_{is}. This discrepancy was explained by assuming a mechanism featuring the formation of a five-membered acyloxonium transition state, whose stability should depend on the nature of the R group [2, 3]. The isomerization of the thiocarboxylic esters of these bromopropanols would lead to the formation of thionecarboxylic acid derivatives if it proceeded through an analogous acyloxonium five-membered sulfur-containing ring. However, such derivatives are not formed. The ^{13}C NMR spectra of the equilibrium mixture of the thioacetates and thiobenzoates of these bromopropanols lack signals for the C=S group.

These results indicate that the replacement of an oxygen atom in the ester group by the much more nucleophilic sulfur atom leads to a change in the isomerization mechanism. The isomerization of the thiocarboxylic esters of these bromopropanols apparently proceeds through a transition state with a three-membered sulfur-containing ring
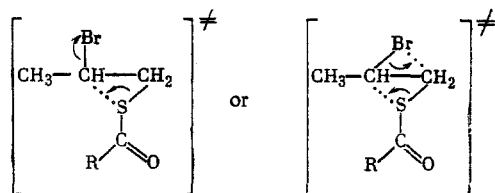
$\dagger[\text{B}]_{\text{eq}} = 0.85$ for calculating k_{is} for (I) and $[\text{B}]_{\text{eq}} = 0.15$ for calculating k_{is} for (II).

CONCLUSIONS

The rate constant for the isomerization of the thioacetates and thiobenzoates of 1-bromo-2-propanol and 2-bromo-1-propanol in aprotic solvents, in contrast to the case for the esters of the corresponding carboxylic acids, is independent of the nature of the group adjacent to the thiocarboxylic group.
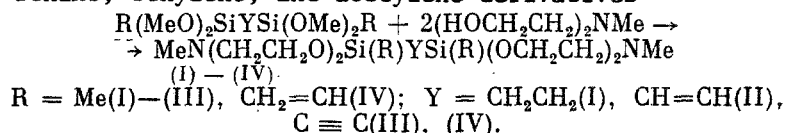
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1,2-BIS(2',6'-DIMETHYL-1',3'-DIOXA-6'-AZA-2'-SILACYCLOOCTYL-2')ETHANE AND THE CORRESPONDING ETHYLENE AND ACETYLENE DERIVATIVES

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In a continuation of a study of cyclic organosilicon ethers of 2-hydroxyalkylamines [1], we synthesized (I)-(IV) by the reaction of bis(2-hydroxyethyl)methylamine with 1,2-bis-(silyl-substituted) ethane, ethylene, and acetylene derivatives

$$R(MeO)_2SiYSi(OMe)_2R + 2(HOCH_2CH_2)_2NMe \rightarrow$$
$$\rightarrow MeN(CH_2CH_2O)_2Si(R)YSi(R)(OCH_2CH_2)_2NMe$$
$$(I) - (IV)$$
$$R = Me(I) - (III), \ CH_2=CH(IV); \ Y = CH_2CH_2(I), \ CH=CH(II),$$
$$C \equiv C(III), \ (IV).$$

Products (I)-(III) are colorless, crystalline compounds, while (IV) is a colorless oil. The yields and melting points of these products are given in Table 1, while the PMR spectra are given in Table 2.

TABLE 1. Characteristics of the Products

Compound	Yield, %	Mp, °C	Chemical formula	Compound	Yield, %	Mp, °C	Chemical formula
(I)	85	55–56	$C_{14}H_{28}N_2O_4Si_2$	(III)	60	150–151	$C_{14}H_{24}N_2O_4Si_2$
(II)	80	94–95	$C_{14}H_{26}N_2O_4Si_2$	(IV)	60	–	$C_{16}H_{24}N_2O_4Si_2$

TABLE 2. PMR Spectra of $MeN(CH_2CH_2O)_2Si(R)YSi(R) \cdot (OCH_2CH_2)_2NMe$ (δ, ppm)

Compound	R	Y	CH_3	CH_2	CH=CH	OCH_2	CH_2N	NCH_3
(I)	Me	CH_2CH_2	0,04 s	0,52 s	–	2,56 m	3,68 m	2,37 s
(II)	Me	CH=CH	0,12 s	–	6,55 s	2,54 m	3,76 m	2,37 s
(III)	Me	$C \equiv C$	0,05 s	–	–	2,47 m	3,67 m	2,31 s
(IV)	$CH_2=CH$	$C \equiv C$	–	–	5,94 m	2,56 m	3,77 m	2,32 s