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Corresponding Member of the Academy of Sciences of the USSR N. I. Shuikin, I. E. Grushko, and I. F. Bel' skii

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Abstract

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ON THE REACTION OF α-METHYLTRIMETHYLENE OXIDE WITH CHLOROSILANES, ALUMINUM CHLORIDE, AND TITANIUM TETRACHLORIDE

Trimethylene oxide, like other organic oxides, reacts with various halogen-containing agents. Hydrogen bromide and phosphorus pentachloride cleave trimethylene oxide with elimination of the oxygen atom and formation, respectively, of 1,3-dibromo- and 1,3-dichloropropanes. Acetyl chloride, reacting with trimethylene oxide, forms γ-chloropropyl acetate ([1]). Searles and co-workers ([2]) investigated the reaction of α-methyltrimethylene oxide with hydrogen halides (HCl, HBr) and acetyl chloride and showed that cleavage of this β-oxide occurs mainly at the C–O bond not adjacent to the methyl group.

In the present work we investigated the reaction of α-methyltrimethylene oxide with several chlorosilanes ($SiCl_4$, CH_3SiCl_3, and $C_6H_5SiCl_3$), aluminum chloride, titanium tetrachloride, and hydrogen chloride. The main purpose of our study was to determine the direction of opening of the β-oxide ring containing an alkyl group in the α-position under the action of various halogen-containing agents. Silicon tetrachloride, methyltrichlorosilane, and phenyltrichlorosilane react with α-methyltrimethylene oxide rather vigorously even at room temperature in the absence of a catalyst. By distillation under reduced pressure, chloro-substituted esters of orthosilicic acid were isolated from the reaction products. The nature of the compounds obtained shows that the reactions proceed according to the following scheme.

$$\text{2-methyloxetane ring} + SiCl_4 \longrightarrow \begin{cases} Cl_3SiOCH_2CH_2CHClCH_3 & (1) \\ ClCH_2CH_2CHOSiCl_3 & \\ \qquad CH_3 & (2) \end{cases}$$

$$\text{2-methyloxetane ring} + CH_3SiCl_3 \longrightarrow \begin{cases} Cl_2(CH_3)SiOCH_2CH_2CHClCH_3 & (1) \\ ClCH_2CH_2CHOSiCl_2(CH_3) & \\ \qquad CH_3 & (2) \end{cases}$$

$$\text{2-methyloxetane ring} + C_6H_5SiCl_3 \longrightarrow \begin{cases} Cl_2(C_6H_5)SiOCH_2CH_2CHClCH_3 & (1) \\ ClCH_2CH_2\underset{\displaystyle CH_3}{CH}OSiCl_2(C_6H_5) & (2) \end{cases}$$

The esters of orthosilicic acid were subjected to hydrolysis; as a result, chlorohydrins were obtained.

The reaction between α-methyltrimethylene oxide and HCl was carried out by passing dry hydrogen chloride through a layer of pure oxide at the boiling temperature of the latter. At the end of the reaction the temperature of the reaction mixture rose, owing to the heat of reaction, to 105–110°.

Aluminum chloride and titanium tetrachloride react so vigorously with α-methyltrimethylene oxide that the reaction between them proceeds satisfactorily only on cooling to −50, −60°. The reaction products were hydrolyzed with water in an ether medium under cooling. As a result of hydrolysis, alcohols containing primarily or secondarily bound chlorine atoms were obtained. In all cases, in the Raman spectra of these chlorohydrins a very strong absorption band was observed at about wave number 660 cm^{-1}, characteristic of a primarily bound chlorine atom ([3]). An absorption band at about wave number 610 cm^{-1}, characteristic of secondarily bound chlorine, was also observed in the spectra, but with much lower intensity. It follows from this that the mixture of chlorohydrins contains predominantly 4-chlorobutan-2-ol. This result leads to the following general conclusion: α-methyltrimethylene oxide, under the action of various halogen-containing agents, is cleaved chiefly at the ether bond not adjacent to the methyl radical. For comparison we note that in the case of unsymmetrical γ-oxides, for example tetrahydrosilvan ([4]), ring opening under the action of chlorosilanes occurs at the C–O bond adjacent to the methyl group.

Experimental Part

α-Methyltrimethylene oxide was obtained according to the following scheme:

$$CH_3\underset{|}{\underset{OH}{CH}}CH_2\underset{OH}{CH_2} \xrightarrow[CaCl_2]{AcCl} CH_3\underset{OAc}{CH}CH_2\underset{Cl}{CH_2} \xrightarrow{KOH} CH_3\text{–}\underset{|}{}O \qquad (^5)$$

Cyclization of 1-chloro-3-acetoxybutane to α-methyltrimethylene oxide was carried out by adding this chloroacetate to molten potassium hydroxide heated to 160–170°; the β-oxide formed was immediately distilled out of the reaction zone. After distillation on a column it had the following properties: b.p. 60° (759 mm), n_D^{20} 1.3900; d_4^{20} 0.8557. Found MR_D 19.97; $C_5H_{10}O$. Calculated MR_D 20.11.

The starting chlorosilanes, on distillation with a dephlegmator, boiled as follows: silicon tetrachloride in the range 58-60°, methyltrichlorosilane at 64-65°, and phenyltrichlorosilane in the range 199-201°.

The reaction between α-methyltrimethylene oxide and silicon tetrachloride, methyltrichlorosilane, and phenyltrichlorosilane was carried out as follows.

α-Methyltrimethylene oxide in an amount of 1 gram-mole was slowly added at room temperature to the halosilane, taken in twofold excess. The reaction proceeded with noticeable heating. After addition of the entire amount of β-oxide, the reaction mixture was heated to boiling for 5-6 hr. The orthosilicic acid esters obtained in about 80% yield were isolated from the reaction products by distillation under reduced pressure. The properties of these esters are given in Table 1. The chloroesters of orthosilicic acid were then subjected to hydrolysis with water. The formation, as a result of this, of two chlorohydrins indicates the formation of two orthosilicic acid esters.

On fractional distillation of the hydrolysis products, a fraction with b.p. 42-45° (5 mm) and n_D^{20} 1.4433 was isolated, which was a mixture of chlorobutyl alcohols. In the literature the following data are available for the isomeric chlorobutanols obtained by us: 4-chlorobutan-2-ol, b.p. 67° (20 mm), n_D^{26} 1.4408 ([5]); 3-chlorobutan-1-ol, b.p. 66-68° (15 mm), n_D^{27} 1.4396 ([6]).

The chlorobutyl alcohols were subjected to acetylation with acetic anhydride. For this, the chlorohydrin and acetic anhydride, taken in double amount, were placed in an Erlenmeyer flask. The mixture was left under ice cooling for 5 hr, and then at room temperature for one day. After distilling off the acetic anhydride that had not entered into the reaction,

the products of acetylation of the anhydride were distilled under reduced pressure. The fraction containing γ-chlorobutyl acetates distilled at 38-41° (6 mm) and had n_D^{20}1.4260. The reaction of α-methyltrimethylene oxide with dry hydrogen chloride was carried out as follows: 1 g-mole of the β-oxide was placed in a flask, and hydrogen chloride was passed through its layer at the boiling temperature of the β-oxide. The reaction usually ended when the temperature of the reaction mixture reached 102°. The latter was then washed with a 5% solution of soda, then with water, after which it was dried with magnesium sulfate and distilled under reduced pressure. The resulting mixture of chlorobutanols was analyzed by the method of combination scattering of light. Aluminum chloride, in portions of approximately 1 g, and titanium tetrachloride from a dropping funnel, also in small portions, were introduced with thorough stirring into α-methyltrimethylene oxide cooled to -50, -60°. After the reaction was complete, ether was added to the reaction mixture, and then hydrolysis with water was carried out under cooling. The chlorobutanols were extracted from the aqueous layer with ether. The ether extracts were washed with soda solution, then with water, dried with potash; after removal of the ether, the chlorobutanols were distilled in vacuo.

The combination-scattering spectra of light were recorded by G. K. Gaivoron-

skaya, for which the authors express their gratitude.

The interaction of α-methyltrimethylene oxide with chlorosilanes, aluminum chloride, titanium tetrachloride, and hydrogen chloride has been investigated. In all cases cleavage of the β-oxide ring proceeds in both possible directions, but predominantly at the ether bond not adjacent to the methyl group. The esters of orthosilicic acid formed as a result of the reaction of α-methyltrimethylene oxide with chlorosilanes are substitution products in which one chlorine atom in the molecule of the starting chlorosilane is replaced by the γ-chlorobutoxyl group.

Table 1

Properties of chlorine-substituted esters of orthosilicic acid

Gross formula of the chloro esters of orthosilicic acid	B.p., °C (mm)	n_D^{20}	Found, % C	Found, % H	Found, % Cl	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Cl	Calculated, % Si
$Cl_3SiOC_4H_8Cl$	56 (5)	1.4403	20.36	3.33	58.21	11.40	19.85	3.30	58.60	11.59
$CH_3SiCl_2OC_4H_8Cl$	39–42 (5)	1.4375	27.90	5.20	47.07	12.23	27.10	5.00	48.00	12.66
$C_6H_5SiCl_2OC_4H_8Cl$	132–136 (8)	1.5062	42.28	4.91	37.31	9.86	42.28	4.62	37.50	9.89

Institute of Organic Chemistry
named after N. D. Zelinsky
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CITED LITERATURE

1. C. G. Derick, D. W. Bissell, J. Am. Chem. Soc., **38**, 2483 (1916).
2. S. Searles, K. A. Pollart, F. Block, J. Am. Chem. Soc., **79**, 952 (1957).
3. K. Kol' raush, *Spectra of Combination Scattering*, Izd., 1952, p. 214.
4. N. I. Shuikin, I. F. Bel' skii, I. E. Grushko, ZhOKh, **29**, 2591 (1959).
5. F. Sondheimer, R. B. Woodward, J. Am. Chem. Soc., **75**, 5438 (1953).
6. R. J. Meltzer, J. A. King, J. Am. Chem. Soc., **75**, 1356 (1953).

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