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REACTION OF HEXAMETHYLDISILOXANE WITH 2-ETHOXY-1,3-DIOXOLANE

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The reaction of hexamethyldisiloxane with 2-ethoxy-1,3-dioxolane is described. It is shown that cleavage of the endo- and exocyclic carbon–oxygen bonds of the ortho ester occurs under mild conditions (16-20°C) in the presence of acidic catalysts with the formation of 2-(trimethylsiloxy)ethyl formate, the subsequent transformation of which leads to ethyl formate, trimethylethoxysilane, and 1,2-bis(trimethylsiloxy)ethane.

The literature contains data on the reaction of acetals and ortho esters with alkoxysilanes [1-4] and 1,3-dioxa-2-silacycloalkanes [5], which proceeds with cleavage of the carbon–oxygen and, correspondingly, silicon–oxygen bonds. Information regarding the reactions of ortho esters with silixanes is not available.

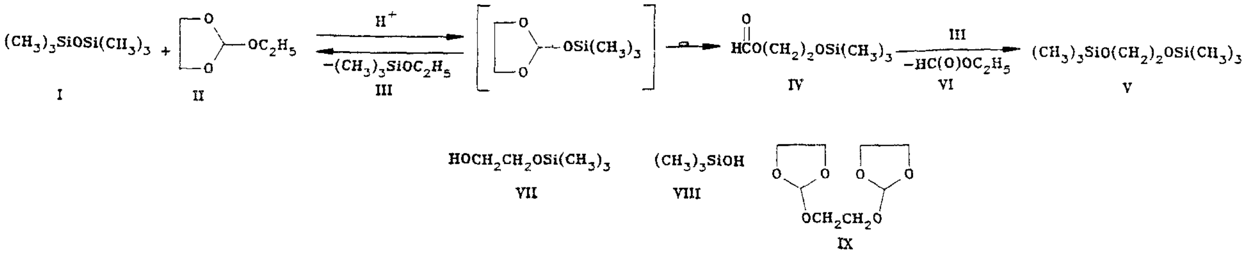
We have studied the acid-catalyzed reaction of hexamethyldisiloxane (HMDS) (I) with 2-ethoxy-1,3-dioxolane (II) for the first time. It was established that the reaction proceeds under mild conditions and leads to the formation of 2-(trimethylsiloxy)ethyl formate (IV), trimethylethoxysilane (III), 1,2-bis(trimethylsiloxy)ethane (V), and ethyl formate (VI).

It is assumed that the initial product is the unstable 2-trimethylsiloxy-1,3-dioxolane, which readily undergoes isomerization to IV. The subsequent reaction of IV and III leads to final products V and VI. According to GLC data, the maximum yield of aldehyde IV is 16-20% and was obtained when phosphorus pentoxide and concentrated nitric acid were used as catalysts (Table 1).

An increase in the temperature from 20°C to 100°C and a change in the molar ratio of the components have virtually no effect on the yield of product IV (Table 1).

Very small amounts (up to 1%) of 2-(trimethylsiloxy)ethanol (VII) and trimethylsilanol (VIII) were detected in the rection mixture by chromatographic mass spectrometry. The formation of the indicated compounds constitutes evidence for partial hydrolysis of the starting compounds and final products:

Scheme 1



(1)

1,2-Bis(1',3'-dioxolan-2'-yloxy)ethane (IX), which may be formed by isomerization of dioxolane II under the experimental conditions [6], is present in trace amounts in the reaction mixture.

It is known that cyclic ortho esters readily undergo isomerization to acyclic compounds under the conditions of solvolysis reactions. Reverse reactions are realized in exceptional bases [6].

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TABLE 1. Conditions and Results of the Reaction of Hexamethyldisiloxane (HMDS) (I) with 2-Ethoxy-1,3-diozolane (II)

Expt. No.	Synthesis conditions				Conversion of the reagents, %		Yields of the compounds (%) according to GLC data			
	molar ratio	time, h	temp., °C	catalyst	I	II	III	IV	V	VI
1	1 : 1	5	100	p-TSA	64	100	27	13	58	60
2	1 : 2	44	20	p-TSA	73	74	27	11	60	62
3	1 : 2	5	50	p-TSA	64	71	24	11	62	65
4	1 : 1	48	20	$SnCl_4$	68	100	17	11	67	72
5	1 : 1	5	70	p-TSA	76	100	28	15	55	57
6	1 : 1	1	20	Conc. H_2SO_4	80	100	26	10	62	64
7	1 : 1	7	20	$AlCl_3$	60	100	17	14	64	69
8	1 : 1	4	20	P_2O_5	78	100	21	16	61	63
9	1 : 1	24	20	Conc. HNO_3	93	100	29	20	49	51
10	1 : 1	1	20	p-TSA	60	100	26	10	62	64

TABLE 2. Mass Spectra of the Principal Components of the Reaction Mixture in the Reaction of I and II

Compound	m/z (peak intensity, % of Σ_{43}*)
II	89 (1), 88 (2), 74 (2), 73 (68), 61 (2), 60 (7), 47 (1), 45 (13), 44 (1), 43 (3)
IV	147 (3), 105 (2), 104 (3), 103 (41), 101 (1), 76 (1), 75 (18), 74 (1), 73 (13), 61 (2), 59 (2), 58 (1), 47 (1), 45 (4), 43 (2)
V	191 (7), 149 (3), 148 (6), 147 (46), 133 (1), 103 (6), 75 (1), 73 (15), 66 (4), 45 (2)
VII	119 (7), 103 (13), 77 (3), 75 (39), 74 (3), 73 (20), 45 (3), 43 (4)
VIII	77 (2), 76 (5), 75 (65), 61 (1), 59 (1), 47 (9), 44 (10), 43 (2)
IX	103 (7), 74 (3), 73 (85), 45 (3), 44 (2)

*The peaks with intensities greater than 1% of Σ_{43} are presented.

Trimethylsilyl ethers are widely used in organic synthesis [7, 8] as compounds with a protected hydroxy group and are characterized by the ease of incorporation and removal of a trimethylsilyl protective group; it therefore seemed of interest to use these properties of the trimethylsilyl group in the synthesis of cyclic ortho esters.

We found that the reaction between ether V and formates VI, X, and XI in the presence of acidic catalysts [H_2SO_4, p-toluenesulfonic acid (p-TSA)] leads to 2-(trimethylsiloxy)-ethyl formate (IV) (13-16% yield) and alkoxysilanes III, XII, and XIII, respectively.

The subsequent transformation of aldehyde IV does not occur, i.e., the corresponding cyclic ortho esters are not formed. A change in the molar ratio of the reagents and removal of the HMDS in order to shift the equilibrium of the reaction also did not lead to synthesis of the ortho ester.

The reaction mixtures of the reactions described above were subjected to chromatographic mass-spectrometric analysis (Table 2). The spectra of I, III, and VI are contained in the library attached to a Finnigan-4021 mass spectrometer. The spectrum of II coincides with the previously published spectrum of 2-ethoxy-1,3-dioxolane [9].

The mass spectrum of 2-(trimethylsiloxy)ethanol (VII) does not contain a molecular-ion peak (M^+). The ratio of the isotope peaks provides evidence for the presence of a silicon atom in the principal fragment ions. The assumption that the first peak in the high-mass region at 119* (Table 2) is the result of splitting out of a methyl group from M^+ seems extremely convincing, since the spectrum in the region of masses below 77 has peaks that are characteristic for a compound that contains a trimethylsilyl or trimethylsiloxy group. Thus, the molecular mass of the compound is 134, and its structural formula is $HOCH_2CH_2OSI(CH_3)_3$. The presence of a terminal hydroxy group is confirmed by the characteristic splitting out of a CH_2OH radical [10] with the formation of an ion at 103. The pathways of the formation of the remaining fragment ions in the spectrum of VII are presented in Scheme 2.

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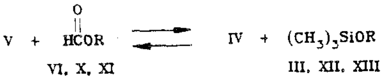
*Here and subsequently, the numbers that characterize the ions are the m/z values.



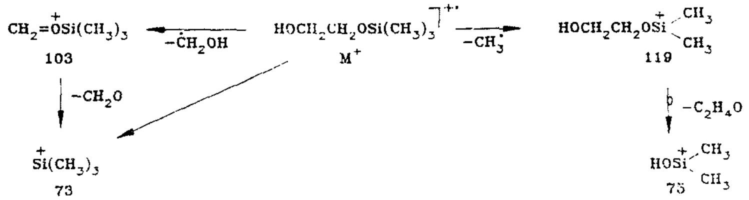
$$\underset{\text{VI, X, XI}}{\mathrm{V} + \overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{H}\mathrm{C}}\mathrm{OR}} \rightleftharpoons \underset{\text{III, XII, XIII}}{\mathrm{IV} + (CH_3)_3SiOR}$$

X, XII R=*s*-C_4H_9; XI, XIII R=C_4H_9

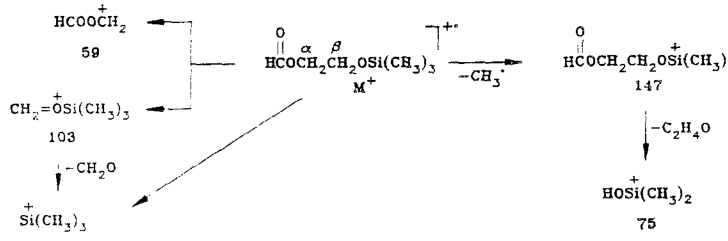
An M^+ peak is abent in the spectrum of 2-(trimethylsiloxy)ethyl formate (VI). The peak of the $[M - CH_3]^+$ fragment ion (147) has a low intensity. The formation of the ion peak at 103, which is the maximum peak in the spectrum, is explained by cleavage of the $C(\alpha)-C(\beta)$ bond in M^+.

In the spectrum of ether V the first significant ion peak with the greatest mass (191) is also due to splitting out of a methyl group from M^+. The appearance of the peak at 147, which is the maximum peak in the spectrum, is associated with skeletal rearrangement of the $[M - CH_3]^{+\cdot}$ ion, which is accompanied by the elimination of a molecule of $(CH_2)_2O$. Different points of view exist relative to the mechanism of rearrangement. Some authors [12, 13] feel that the intramolecular reaction with cyclization of the $[M - CH_3]^+$ ion occurs, while Koppel and coworkers [14] dispute the cyclic structure of this ion.

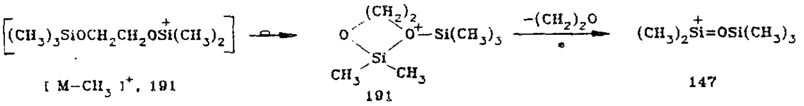
Scheme 2



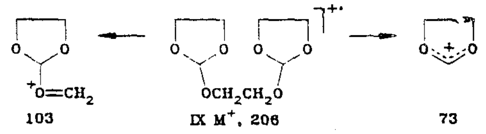
Scheme 3



Scheme 4



Scheme5



In our opinion, the presence of a peak of a metastable ion corresponding to the 191 → 147 transition [13] in the spectrum of 1,2-bis(trimethylsilyl)ether V is of the greatest significance.

The mass spectrum of IX provides evidence for the high selectivity of the fragmentation processes, since two ions – those with m/z 103 and 73 – provide virtually all of the ion current in the spectrum (Table 2).

An analysis of the mass spectrum of (sec-butoxy)trimethylsilane (XII) revealed, as expected, characteristic features of the fragmentation that are peculiar to silyl ethers of aliphatic alcohols [11, 15].

EXPERIMENTAL

The analysis of the starting compounds and final products was carried out by GLC with a Tsvet-102 chromatograph with a thermal-conductivity detector (3 m × 3 mm column, 5% SE-30 on

Chromaton N-AW silanized with HMDS, helium as the carrier gas, flow rate 1.5 liters/h). The starting reagents were fractionated by distillation, while the reaction products are isolated with a PAKhV-08 preparative chromatograph (2 m × 9 mm column, 5% SE-30 on Chromaton N-AW silanized with HMDS, helium as the carrier gas, flow rate 9 liters/h, vaporized with HMDS, helium as the carrier gas, flow rate 9 liter/h, vaporizer temperature 200°C, collector temperature 200°C, thermostat temperature 77°C).

The PMR spectra of 10% solutions in CCl_4 were recorded with a Tesla-497 spectrometer with $CHCl_3$ as the internal standard.

The chromatographic mass spectra were recorded with a Finnigan-4021 spectrometer. The operating conditions were as follows: T_{vap} = 280°C, linear programming of the thermostat temperature at a rate of 5°C/min, T_{in} = 50°C, T_{fin} = 200°C, 50 m by 0.25 mm steel capillary, VR-1 phase helium flow rate 3 cm^3/min, and ionization energy 70 eV.

The results of elementary analysis of IV and V for C, H, and Si were in agreement with the calculated values.

A 0.175-g (1.784 mmole) sample of concentrated H_2SO_4 was added to a mixture of 2.1 g (18 mmole) of 2-ethoxy-1,3-dioxolane and 2.8 g (18 mmole) of HMDS (the pH of the mixture was 2), after which the reaction mass was stirred vigorously for 1 h by means of a magnetic stirrer and then neutrlized to pH 7 with triethylamine. Reaction products III-VI were fractionated at atmospheric pressure and purified with a PAKhV-08 preparative chromatograph.

2-(Trimethylsiloxy)ethyl Formate (IV, $C_6H_{14}O_3Si$). This compound was obtained in 13.6% yield and had n_D^{20} 1.4087, d_4^{20} 0.90608, and MR_D 41.72 (calculated value 41.82). PMR spectrum 0.02 [9H, s, $(CH_3)_3Si$], 3.63 [2H, t $-CH_2-O-Si$], $^3J_{H,H}$ = 5.1 Hz); 4.06 (2H, t, $O-CH_2-$, $^3J_{H,H}$ = 5.1 Hz); 8.01 ppm (H, s, HCO_2).

1,2-Bis(trimethylsiloxy)ethane (V, $C_8H_{22}O_2Si_2$). This compound had bp 165°C (760 mm), n_D^{20} 1.3995; d_4^{20} 0.8265, and MR_D 60.48 (calculated value 20.81). PMR spectrum: 0.02 [18H, s, $(CH_3)_3Si$], 3.51 ppm (4H, s, CH_2-O).

A 0.117-g (1.193 mmole) sample of concentrated H_2SO_4 was added to a mixture of 2 g (28 mmole) of ethyl formate and 5.8 g (18 mmole) of 1,2-bis(trimethylsiloxy)ethane (the pH of the mixture was 2), after which the reaction mass was stirred vigorously for 30 min by means of a magnetic stirrer and then neutralized to pH 7.0 with triethylamine. Reaction products III and IV were fractionated at atmospheric pressure and purified with a PAKhV-08 preparative chromatograph.

The physicochemical constants of IV, VI, and VII were in agreement with the literture data [7, 16, 17].

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INTENSITIES OF IR BANDS OF CH STRETCHING VIBRATIONS AND ATOMIC CHARGES IN SATURATED THREE-MEMBERED RINGS

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The intensities of the absorption bands of the CH stretching vibrations in the IR spectra of solutions of cyclopropane, aziridine, oxirane, and thiirane in CCl_4 were measured. Quantum-mechanical calculations of these intensities were performed.

Attempts have been made in recent years to use data on the intensities of absorption bands in IR spectra to determine the charges on the atoms in molecules or organic compounds [1-7]. The fundamental possibility of obtaining information regarding the charges on the atoms from IR spectroscopic data is based on the modern interpretation of the behavior of vibrating molecules, which establishes a relationship (in analytical form) between the parameters of the electrooptical field and the characteristics of the distribution of the electron density on atoms or in bonds [1; 8, p. 155]. A limited number of charges on atoms found from the absolute intensities of the IR spectra (chiefly for simple hydrocarbons and halo-substituted methanes; for example, see [1]) are currently known. The charges on the atoms in the molecules of these compounds thus obtained are completely reasonable, and the data on the tendency of their change as a function of the type of chemical bond coincide with the data obtained by other methods. The complexity of distinguishing the individual bands in the IR spectra from the absolute intensities hinders the more extensive incorporation of the method of determining the charges based on a knowledge of the intensities. The intensities of the bands in the IR spectra the solutions of organic substances in inert solvents are of interest for expanding the possibilities of the use of IR spectroscopy in the study of the problem of the distribution of the electron density in molecules. The expedience of resorting to solutions is determined by the fact that nonvolatile compounds, for which recording of the IR spectra in the gaseous state is virtually impracticable, can be subjects of investigation in this case. In addition, the absence of resolution of the fine structure of the IR bands makes it possible to avoid the use of high pressures. As regards the effect of the solvent on the IR intensities, it is eliminated to a considerable extent if one is interested not in their absolute values but only in the course of the change in a certain series of compounds.

At the present time a great deal of data on the intensities of the bands of CH stretching vibrations (A_i) in the IR spectra of solutions of series of substituted methanes [9, 10], ethylenes [11], and acetylenes [12] has been accumulated. In interrelationship between the A_i^{soln} values found and the empirical characteristics of reactivity has been traced in order to ascertain general structural and spectrochemical principles [9-12]. Moreover, the question as to whether the actual charge distribution corresponds to the principles that are characteristic for the intensities of the IR spectra was not examined in [9-12].

In the present research the investigation of the intensities of the bands of the IR absorption spectra in the region of CH stretching vibrations was extended to solutions of saturated three-membered rings. The specific characteristics of these molecular systems are due to the ring strain peculiar to them and to the existence of interaction of the CH bonds with the ring heteroatom. The research pursues three interrelated goals:

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