HOMOLYTIC ADDITION OF TETRAHYDROFURAN AND 1,4-DIOXANE TO TRIALKYL- AND TRIETHOXY(VINYL)SILANES

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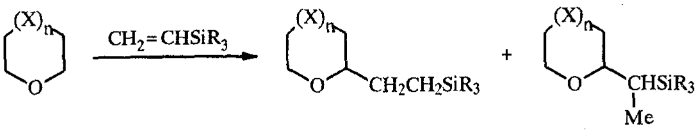
A convenient method for the initiation by oxygen of homolytic reactions of tetrahydrofuran with trimethyl-, triethyl-, and triethoxy(vinyl)silane is proposed. Previously undescribed organosilicon derivatives of 1,4-dioxane and dibutyl ether were synthesized.

It is known that some organosilicon compounds have defoliating activity [1, 2]. In order to synthesize new organosilicon ethers — potential plant-growth regulators — and to continue our research on the homolytic addition of ethers to various types of C=C bonds [3, 4] we studied the reactions of tetrahydrofuran (I) and 1,4-dioxane (II) with trimethyl-, triethyl-, and triethoxy(vinyl)silane (IIIa-c, respectively) under conditions of initiation using autoxidation or di-tert-butyl peroxide (DTBP). To ascertain the effect of the cyclic character of the structure of the ether on its reactivity we investigated the addition of an acyclic ether — dibutyl ether (IV) — to silane IIIa.

The addition of ether I to vinylsilanes IIIa, b in the presence of DTBP [5] was previously described in [5]; these reactions with ethers II and IV were not studied.

For the initiation of the reactions of ethers I and II with silanes we used oxygen, which was previously recommended as a convenient, cheap, and effective initiator of the homolytic cyanoethylation of ether I [6]. The initiation of the process occurs as a result of decomposition of the cyclic ether hydroperoxide formed in the oxidation of the ether. The reactions were carried out in an autoclave with a manyfold excess of the addend; organosilicon ethers Va-c and VIIa-c were obtained. Products VIa and VIIIa of addition in accordance with the Markownikoff rule, which are formed in low yields (3-4%) and were identified by means of their PMR spectra, were detected along with the indicated adducts when silane IIIa was used. Products of oxidation of cyclic ethers I and II were detected in addition to the adducts. Thus γ-butyrolactone and α-hydroxytetrahydrofuran (the yield does not exceed 2% of the cyclic ether used in the reaction) were identified in the case of ether I.



Va-c; IIa-c

VIa, VIIIa

X = O; Va-c, VIa n = 0; VIIa-c, VIIIa n = 1; Va—VIIIa R = Me; Vb, VIIbR = Et;
Vc, VIIcR = OEt

It is apparent from the results (Table 1) that oxygen proved to be a quite effective initiator of the addition of cyclic ether I to vinylsilanes IIIa-c, particularly at a reaction temperature of 200°C in the case of the reaction of I with silane IIIa (experiment 1), although a significant amount of adduct Va is also formed at a lower temperature (130°C) (experiment 2). An adduct was not detected in an inert gas at 130°C. A change in the ratio of the starting compounds within the limits 1:100-30 decreases the yield of Va sharply because of the occurrence of telomerization and polymerization processes (experiments 2 and 3). An experiment carried out under milder conditions at the boiling point of cyclic ether I (66°C) in a sealed apparatus in the presence of $Co(OAc)_2 \cdot 4H_2O$ showed that the yield of adduct Va is low (experiment 4). The $Co(OAc)_2 \cdot 4H_2O$ was used

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1606-1610, December, 1992. Original article submitted February 10, 1992.

0009-3122/92/2812-1374$12.50

TABLE 1. Homolytic Addition of I, II, and IV to Trialkyl- and Triethoxy(vinyl)silanes $CH_2{=}CHSiR_3$*

Expt. No.	R	Ether	Initiator	Vinylsilane: ether:initiator molar ratio	T, °C	Yield, %
1	Me	I	O_2	1 : 100	200	62 (Va)
2	"	I	"	1 : 100	130	46 (Va)
3	"	I	"	1 : 30	130	6 (Va)
4**	"	I	O_2 + $Co(OAc)_2 \cdot 4H_2O$	1 : 70 ($3{,}4 \cdot 10^{-3}$)	66	11 (Va)
5	Et	I	O_2	1 : 100	200	40 (Vb)
6	OEt	I	"	1 : 100	200	29 (Vc)
7	Me	II	"	1 : 100	200	14 (VIIa)
8	"	II	DTBP	1 : 100 : 0,1	200	42 (VIIa)
9	"	II	"	1 : 100 : 0,1	135	11 (VIIa)
10	"	II	"	1 :30 : 0,1	135	4 (VIIa)
11	Et	II	"	1 : 100 : 0,1	200	31 (VIIb)
12	OEt	II	"	1 : 100 : 0,1	200	13 (VIIc)
13***	Me	IV	"	1 : 100 : 0,1	200	4(IX)

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*The experiments were carried out in an autoclave for 4 h.

**This experiment was carried out in an sealed apparatus for 5 h.

***Compounds X and XI were obtained in 3% and 13% yields, respectively.

to accelerate the oxidation of tetrahydrofuran and the decomposition of tetrahydrofuran hydroperoxide, since in the absence of this salt the rates of these processes are low, and the reaction does not take place.

The addition of six-membered cyclic ether II to vinylsilanes IIIa-c proceeds with greater difficulty. It is known that for cyclic ethers the ease of detachment of the α-H atom by the initiating radicals is determined not only by the presence of oxygen in the ring but also by the size of the ring itself [7]. The method of initiation has a substantial effect on the yield of adduct VIIa. Oxygen proved to be less effective in the reaction of ether II with silane IIIa than in the case of the reaction of I with IIIa. This can be explained by the fact that ether II is oxidized with greater difficulty as compared with ether I, while dioxane hydroperoxide decomposes more slowly than tetrahydrofuran hydroperoxide. Adduct VIIa is formed in considerably greater amounts in the presence of DTBP (experiments 7 and 8). An increase in the reaction temperature (experiments 8 and 9) and an increase in the ratio of the starting compounds (experiments 9 and 10) promote an increase in the yield of VIIa.

In contrast to cyclic ethers, dibutyl ether reacts with vinylsilane IIIa to give a complex mixture of products and adduct IX in low yield.

$$(C_4H_9)_2O + CH_2{=}CHSiMe_3 \longrightarrow \underset{\text{IX}}{C_3H_7CH(OC_4H_9)CH_2CH_2SiMe_3} +$$

$$+ \underset{\text{X}}{C_5H_{11}SiMe_3} + \underset{\text{XI}}{C_3H_7C(O)CH_2CH_2SiMe_3} + C_3H_7CHO$$

It is known that the α-butoxybutyl radical formed in the initiation step is unstable and decomposes to give butyraldehyde and a butyl radical [8], which can participate in subsequent transformations to give various products.

It was established that the yields of adducts Va-c and VIIa-c depend not only on the nature of the ether but also on the vinylsilane used, the reactivity of which is determined by the substituents attached to the silicon atom. The addition of ethers to vinylsilane IIIa proceeds most readily. The steric effect of ethyl and ethoxy groups probably decreases the reactivities of silanes IIIb, c (experiments 1 and 5 and 6; experiments 8 and 11 and 12). Products of addition in accordance with the Markownikoff rule evidently are also not formed for the same reason. The lower yields of adducts Vb, c and VIIb, c as compared with Va and VIIa may also be due to chain transfer by the ethyl and ethoxy groups of the monomer and polymer. The reaction mixtures of IIIc with ethers I and II contain significant amounts of polymers.

Thus the results of the investigation showed that cyclic ethers I and II react considerably more readily with the investigated vinylsilanes than acyclic dibutyl ether. However, five-membered ether I greater activity in reactions involving

TABLE 2. Characteristics of the Synthesized Compounds

Compound	Empirical formula	bp, °C (mm)	PMR spectrum, δ, ppm*			Mass spectrum, m/z (I, %)
			ring protons		other protons	
			α-H	β-H		
Va*	$C_9H_{20}OSi$	67...68(2)	3,7 m (3H)	2,05 m (4H)	1,4 m (2H,CH_2)	157 (M^+-CH_3, 29), 127 (41), 101 (37), 99 (22), 75 (68), 73 (100), 71 (88)
Vb**	$C_{12}H_{26}OSi$	80...81(2)	3,8 m (3H)	1,7 m (4H)	1,3 m (2H,CH_2)	186 (M^+-C_2H_4, 25), 185 (100), 157 (44), 129 (50), 117 (38), 115 (38), 103 (95), 99 (45), 71 (50)
Vc	$C_{12}H_{26}O_4Si$	97...98(4)	4,3 m (3H)	2,6 m (4H)	2,2 m (2H,CH_2)	216 (M^+-OC_2H_5, 10), 188 (52), 163 (40), 119 (34), 87 (95), 71 (100)
VIa	$C_{12}H_{26}OSi$	—	3,8 m (3H)	1,9 m (4H)	0,4 m (1H,SiCH) 1,05 m (3H,CH_3)	—
VIIa	$C_9H_{20}O_2Si$	102...103(2)	3,5 m (3H)	3,5 m (4H)	1,4 m (2H,CH_2)	173 (M^+-CH_3, 82), 129 (21), 115 (23), 101 (100), 87 (28), 73 (98), 58 (23), 55 (89)
VIIb	$C_{12}H_{26}O_2Si$	120...121(2)	3,5 m (3H)	3,5 m (4H)	1,35 m (2H,CH_2)	202 (M^+-C_2H_4, 15), 201 (100), 143 (10), 129 (46), 115 (11), 101 (21), 87 (26)
VIIc	$C_{12}H_{26}O_5Si$	129...130(3)	3,5 m (3H)	3,5 m (4H)	1,55 m (2H,CH_2)	233 (M^+-OC_2H_5, 33), 191 (14), 188 (13), 177 (11), 163 (100), 119 (33), 101 (12), 87 (22), 73 (100), 55 (20)
VIIIa	$C_9H_{20}O_2Si$	—	3,6 m (3H)	3,6 m (4H)	0,5 m (1H,SiCH) 1,0 m (3H,CH_3)	—
IX	$C_{13}H_{30}OSi$	—	—	—	1,45 m (10H,CH_2); 1,0 m (6H,CH_3); 3,45 m (3H,$CHOCH_2$)	215 (M^+-CH_3, 8), 187 (9), 157 (7), 128 (28), 101 (12), 73 (100)
X	$C_8H_{20}Si$	—	—	—	1,3 m (6H,CH_2); 1,0 m (3H,CH_3)	129 (M^+-CH_3, 88), 101 (84), 87 (27), 73 (100), 58 (8)
XI	$C_9H_{20}OSi$	61...62(2)	—	—	1,55 m (2H,CH_2); 1,05 m (3H,CH_3); 2,4 m (4H,CH_2CO)	157 (M^+-CH_3, 100), 143 (44), 129 (56), 101 (17), 87 (13), 73 (14)

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*$SiCH_3$ (δ, ppm) 0.00 s (CH_3); $SiCH_2CH_3$ (δ, ppm) 0.2-0.4 q (CH_2), 0.6-0.9 t (CH_3); $SiOCH_2CH_3$ (δ, ppm) 3.5-4.0 q (OCH_2), 1.0-2.0 t (CH_3).

**According to [5], Va had bp 112-113°C (8), and Vb had bp 70°C (1).

addition to silanes under autoxidation conditions than six-membered ether II. Oxygen is proposed as a quite effective initiator of homolytic addition of tetrahydrofuran to trimethyl-, triethyl-, and triethoxyvinylsilane. The possibility of the synthesis of organosilicon derivatives of 1,4-dioxane was demonstrated.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a JNMC-60GL spectrometer; hexamethyldisiloxane (HMDS) was used as the internal standard for Vb, c and VIIb, c, while the spectra of V-VIIIa and IX-XI were recorded without an internal standard by taking the signal of the $SiCH_3$ group as 0 ppm. The mass spectra were obtained with an MKh-1303 spectrometer with a system for direct introduction into the ion source at an ionization energy of 70 eV. Analysis by GLC was carried out with a Biokhrom-1 chromatograph; the detector was a catharometer, the carrier gas was helium, the liquid phase (lucoprene) was applied in 5% amounts to Inerton Super, the column dimensions were 2000 by 3 mm, and the column temperature was programmed from 50°C to 250°C at a rate of 8 deg/min.

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

2-[β-(Trimethylsilyl)ethyl]tetrahydrofuran (Va), 2-[β-(Triethylsilyl)ethyl]tetrahydrofuran (Vb), 2-[β-(Triethoxysilyl)ethyl]tetrahydrofuran (Vc), and 2-[α-Methyl-α-(trimethylsilyl)methyl]tetrahydrofuran (VIa). A. The air was evacuated from an autoclave to a residual pressure of 2 mm, and the autoclave was purged with an inert gas two to three times; the gas was evacuated again after each purging. The autoclave was then charged with a reaction mixture consisting of 12 moles of tetrahydrofuran and 0.12 mole of vinylsilane IIIa-c, and the residual volume was filled with oxygen up to atmospheric pressure. The coefficient of charging of the autoclave was 0.5. The autoclave was heated for 4 h. At the end of the reaction, the excess starting ether was removed by distillation, the residual concentrated reaction mixture was analyzed by GLC, and the adduct was then isolated by fractional distillation in vacuo (see Table 2).

B. Oxygen (0.089 mole) was passed for 1.5 h at 66°C through a mixture of 360 g (5 moles) of tetrahydrofuran and 0.8 g ($3.4 \cdot 10^{-4}$ mole) of $Co(OAc)_2 \cdot 4H_2O$. The passage of oxygen was then discontinued, and a solution of 10.03 g (0.1 mole) of trimethyl(vinyl)silane in 144 g (2 moles) of tetrahydrofuran was added in the course of 3 h, after which the reaction mixture was refluxed for another 30 min.

2-[β-(Trimethylsilyl)ethyl]dioxane (VIIa) and 2-[α-Methyl-α-trimethylsilyl)methyl]dioxane (VIIIa). These compounds were obtained under autoxidation conditions by method A.

2-[β-(Triethylsilyl)ethyl]dioxane (VIIb) and 2-[β-(Triethoxysilyl)ethyl]dioxane (VIIc). These compounds were obtained under conditions of initiation of the reaction by di-tert-butyl peroxide (DTBP). The method used to carry out the experiment was similar to method A, except that the residual volume of the autoclave after charging of the reaction mixture was filled with helium. The composition of the reaction mixture was as follows: 12 moles of 1,4-dioxane, 0.12 mole of vinylsilane IIIb or IIIc, and 0.012 mole of DTBP.

α-Trimethylsilyl-γ-butoxyhexane (IX), α-Trimethylsilylpentane (X), and α-Trimethylsilyl-3-hexanone (XI). These compounds were obtained in the same way as VIIb, c. Products IX-XI were separated by chromatography with a column packed with L 100/160 μ silica gel with successive elution with hexane, hexane—acetone (with a gradual increase in the amount of acetone), and acetone.

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