RADICAL TELOMERIZATION OF TRIMETHYLVINYLSILANE BY METHYL ESTERS OF CARBOXYLIC ACIDS

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The use of trimethylvinylsilane (TVS) and other heteroorganic unsaturated compounds as monomers in the radical telomerization with carboxylic acid esters opens a new path for the preparation of heteroorganic telomers containing a carbofunctional group and a chain of atoms, including the element—carbom bond, in the molecule. Comparison of the results obtained during the study of telomerization of TVS with methyl propionate (MP), methyl isobutyrate (MIB) and methyl bromoacetate (MBA) showed substantial influence of the nature of the telogen and the reaction conditions on the composition of the reaction mixture and the character of the compounds formed, and this was the subject of the present work.

In the case of methyl propionate [1, 2], telomer—homologs are formed having the structrue $H(Me_3SiCHCH_2)_nCHMeCO_2Me$ (T_n) (I) (Table 1) according to normal telomerization procedure. Among telomers with two monomeric units, compounds $(Me_3SiCH_2CH_2)_2CMeCO_2Me$ ($T_2{}^1$) was identified by ^{13}C NMR. Its formation can involve rearrangement of the growing radicals with a 1,3-migration of the H atom [2]. It has previously been shown that the reaction of propylene with MP proceeds in a similar way [3].

In the reaction of TVS with MIB, we can expect the formation of only one type of telomer $H(Me_3SiCHCH_2)_mCMe_2CO_2Me$ (T_m), since the absence of an H atom at the α-C atom in the growing radicals excludes the possibility of isomerization occurring

$$Me_2CHCO_2Me \xrightarrow{RO^{\cdot}} Me_2\dot{C}CO_2Me$$

$$Me_2\dot{C}CO_2Me + mMe_3SiCH{=}CH_2 \xrightarrow{HD} T_m \quad (m = 1, 2)$$

However, besides the telomers T_m (m = 1, 2) (II), (III), see Table 1), a further compound was isolated from the reaction mixture, for which, according to the data of ^{13}C NMR spectra, the structure of $Me_3SiCH_2CH{=}CHCH_2CMe_2CO_2Me$ ($T_2{}^H$) ((IV), Table 1) was proposed. An unsaturated compound can form, for example, by the thermal decomposition of the part of T_2 with splitting of the internal Me_3Si group. The possibility of this path of formation of $T_2{}^H$ is principally indicated by the comparison of the results of experiments 5 and 4 (Table 2) carried out at 60 and 140°C, respectively. In the first case the ratio $T_2{}^H/(T_2{}^H + T_2)$ is 0.19, while at a higher temperature, it increases to 0.44. The partial chain transfer constant for the first growing radical, $Me_3SICHCH_2CMe_2CO_2Me$, estimated to be in the range M/S = 0.9-0.42 (see Table 2), is $C_1 \cong 0.3$. This value is close to that obtained for the telomerization of propylene by MIB ($C_i = 0.28$) [4]. A further increase in the TVS concentration leads to an increase in C_1 (see Table 2), possibly due to the enhancement of the role of TVS as a hydrogen donor (HD).

The similarity of the behavior of TVS and propylene in the telomerization is a reflection of the similarity of their polar characteristics and the stability of the radical center adjacent to the Me_3Si and CH_3 groups. The considerable influence of the polar nature of the substituents at the Si atom on the reactivity of vinylsilanes in the radical reactions, and also the similarity of the influences of the CH_3 and Me_3Si groups on the course of reaction, has already been noted in several cases [5, 6]. The reaction of TVS with a highly effective telogen such as MBA, which react at the C—Br bond, practically stops at the stage of addition with the formation of adduct (V) (see Table 1).

$$CH_2BrCO_2Me + Me_3SiCH{=}CH_2 \xrightarrow{DBr} \underset{(T_1{}^c)\qquad(V)}{Me_3SiCHBrCH_2CH_2CO_2Me}$$

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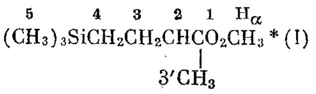
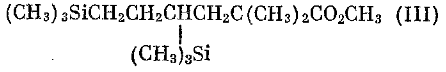
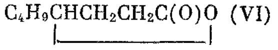
TABLE 1. Physicochemical Characteristics of Isolated Compounds

Compound	n_D^{20} (d_4^{20})	Found/calc., %			^{13}C NMR spectra (δ, ppm, referred to TMS)			
		C	H	Si	CO_2	C, CH	CH_3	CH_2
 $\overset{5}{(CH_3)_3}Si\overset{4}{CH_2}\overset{3}{CH_2}\underset{3'CH_3}{\overset{2}{CH}}\overset{1}{CO_2}\overset{H_\alpha}{CH_3}$* (I)	1,4252 (0,8693)	57,55/57,45	10,77/10,64	15,07/14,89	176,1	41,9	50,8(α), 16,1(3), −2,4(5)	27,9(9) 13,6(4)
$(CH_3)_3SiCH_2CH_2C(CH_3)_2CO_2CH_3$ (II)	1,4267 (0,8598)	59,35/59,41	10,70/10,89	14,08/13,86	177,7	43,3	51,0(α), 24,4(3), −2,2(5)	34,8(3) 11,1(4)
 $(CH_3)_3SiCH_2CH_2\underset{(CH_3)_3Si}{CH}CH_2C(CH_3)_2CO_2CH_3$ (III)	1,4503 (0,8693)	59,88/59,60	11,52/11,26	19,53/18,54	176,7	42,5(2) 24,5(4)	50,8(α), 24,7(3), −1,9(5), −2,1(7)	39,8(3) 26,7(5) 15,9(6)
$(CH_3)_3SiCH_2CH{=}CHCH_2C(CH_3)_2CO_2CH_3$ (IV)	–	–	–	–	176,0	129,2(4) 124,0(5) 42,2(2)	50,8(α), 24,7(3), −2,1(7)	43,6(3) 22,7(6)
$(CH_3)_3SiCHBrCH_2CH_2CO_2CH_3$ (V)	1,4693 (1,1774)			11,1/11,0	171,6	42,8	50,9(α), −3,1(5)	32,9(2) 28,4(3)
 $C_4H_9CHCH_2CH_2C(O)O$ (VI)	–	–	–	–	174,6	79,3	13,8	35,3(5) 28,2(2) 27,8(3) 27,3(6) 22,3(7)

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*For telomers with two monomeric units, see [1].

TABLE 2. Telomerization of Trimethylvinylsilane with Methyl Isobutyrate (140°C, PTB)

No.	Charge, mmoles		Conversion,* %, M	M/S_{mean}	Distribution of telomers, moles % per total of telomers				C_1 †
	M	S			T_1	T_2^H	T_2	$\Sigma T_n > 2$	
1	1,2	11,1	22,9	0,09	72,3	9,6	14,2	3,9	0,24
2	1,9	14,7	10,5	0,12	66,5	13,6	16,1	3,8	0,24
3	1,9	11,8	27,5	0,14	65,9	14,1	17,6	2,3	0,27
4	1,9	9,8	30,3	0,18	62,5	15,3	19,3	2,9	0,30
5‡	1,9	9,8	19,6	0,17	15,3	8,1	33,5	43,1	
6	1,9	5,9	22,8	0,29	59,2	16,4	21,3	3,1	
7	1,9	3,9	25,8	0,42	50,3	24,5	23,0	2,2	0,43
								C_1 mean	=0,32± ±0,07

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*Conversion of telogen 1-3%; [PTB] = 1-2%, 1 h.

†In experiments with $M/S \simeq 0.6$, the value of $C_1 = 0.6$ was obtained.

‡The experiment was carried out in the presence of dicyclohexyl peroxycarbonate at 60°C.

In this case the influence of the nature of the initiating system on the course of the reaction was unusual. In the preparative experiments ($M/S \sim 0.3$; PB; 90°C), T_1^C is formed in good yield (30-50% based on charged telogen), which is close to the literature data [7]. With PTB (140°C), the reaction proceeds much more poorly (Table 3). The use of complex initiators based on Mn and Fe carbonyls taken at low concentrations (0.4-0.8 mole %) was also relatively ineffective. At initiator concentrations higher by one order of magnitude (4-8 mole %) there is a sharp difference between the two. $Mn_2(CO)_{10}$ at 140°C promotes the addition as effectively as PB at 90°C, while in the presence of $Fe(CO)_5$ no adduct is formed.

It is known that $Mn_2(CO)_{10}$, $Fe(CO)_5$ and systems based on them are effective initiators of the radical telomerization of unsaturated compounds by chlorine-substituted acetic acids, reacting as the result of rupture of the C—Cl bond [8]. One of the possible explanations for the ineffectiveness of $Fe(CO)_5$ is the inhibition thereof by the Br atoms formed from MBA at high temperature.

Similar results for MBA have been previously observed in [9]. Adduct T_1^C was purified by means of preparative GLC using an evaporator and a stainless steel column. Under similar conditions, from the mixture obtained in the reaction of MBA with 1-hexene, in which an adduct with the structure $BuCHBrCH_2CH_2CO_2Me$ should have been formed, only the corresponding lactone (VI) was isolated (see Table 1), the structure of which was established from the data of the ^{13}C NMR spectra. In the case of the reaction of MBA with 1-hexene, the main characteristics of the influence of the nature of the initiating system are the same as for TVS. The structure of all the compounds which were isolated was confirmed by the data of ^{13}C and ^1H NMR spectra. For esters of branched carboxylic acids (I)-(V), the signals of the CO_2, CH_3O, $^{13}CH_3C$ and $^{13}CH_3CH$ groups were characteristic; the monomer fragments are represented by the signals of the CH_3Si and $SiCH_2$ groups [10] occurring in a strong field uncharacteristic of the methylene group. The presence of the Br atom in SiCHBr grouping leads to a shift of the corresponding signal to the weak field. To assign the signals, in several cases spectra were run without suppression of the interaction with protons, and also by using the "DEPT" technique. The chemical shifts and the intensities of the signals in the ^1H NMR spectra correspond to the structure proposed for the compounds listed in Table 1. The structure of the unsaturated telomer T_2^H (IV) is confirmed by the presence in the spectrum of carbon signals in the CH=CH group and by the downfield shift of the ^{13}C signal in the $SiCH_2$ group under the influence of the neighboring double bond. The ratio of the signal intensities corresponds to the assignment which was made. The structure of lactone (VI) also agrees well with the data of the ^1H and ^{13}C NMR spectra (see Table 1), in particular, the absence of the CH_3O and CHBr group signals and the apppearance of the OCH signal in the characteristic region; the remaining signals correspond to the assignments made.

TABLE 3. Addition of Methyl Bromoacetate (S) to Trimethylvinylsilane (M) and 1-Hexene (M) (M/S ∿ 1, τ = 1 h, standard — amyl benzoate)

No.	Initiator, mole %, based on MBA	Conversion		T, °C	Content of reaction products, % based on charged telogen		
		M	S		adduct	lactone	dimer
			MBA–TVS				
1	PB, 5		35	90	21,0	—	—
2	PTB, 5	—	5	140	3,2	—	—
3	$Mn_2(CO)_{10}$, 0,4	—	7	140	5,7	—	—
4	$Mn_2(CO_{10})$, 4,0	—	51	140	21,8	—	—
5	$Mn_2(CO)_{10}$, 0,4 DMFA, 40	—	33	140	10,8	—	—
6	$Fe(CO)_5$, 0,8	—	3	140	—	—	—
7	$Fe(CO)_5$, 8	—	10	140	—	—	—
8	$Fe(CO)_5$, 8 DMFA, 40	—	11	140	—		
			MBA–1-hexene				
9	PB, 5		10,0	140	5,1	4,6	—
10	PTB, 5		5	140	1,3	1,0	—
11	$Mn_2(CO)_{10}$, 4	56,4	48,2	140	8,6	—	3,4
12	$Mn_2(CO)_{10}$, 4 DMFA, 40	57,1	45,9	140	8,8	—	3,9
13	$Fe(CO)_5$, 8	30,3	46,5	140	—	1	—
14	$Fe(CO)_5$, 8 DMFA, 40	50,5	49,9	140	—	1	—

EXPERIMENTAL

^{13}C NMR spectra were run on a "Bruker WP-200" spectrometer, using CCl_4 as the internal standard. The GLC analysis was carried out on a LKhM-8MD-5 chromatograph, using a 3 × 2000 mm column with 5% SE-30 on Chromaton N-AW, katharometer, He carrier gas; preparative GLC; 9 × 1200 mm column with 15% E-301 on Chromaton N-AW, 150-200°C.

Telomerization of Trimethylvinylsilane by Methyl Isobutyrate. The preparative experiments were carried out in sealed 30 ml glass ampules, previously evacuated and filled with nitrogen. The ampules with the starting compounds (12.8 g of MIB, 2.5 g of TVS, and 1 g of PTB) were placed in metal cartridges and heated on an oil bath for 2 h at 140°C with agitation of the reaction mixture by means of rotation.

The reaction mixtures from 4 ampules were combined and the unreacted starting compounds were distilled off; the residue (12 g, 24% based on MIB charged) was divided into narrow fractions, from which telomers (II)-(IV) were isolated by preparative GLC (see Table 1). The dimer $(Me_2CCO_2Me)_2$, PMR spectrum [(δ, ppm, with reference to TMS): 3.64 (3H, CH_3O) and 1.22 (6H, CH_3)], and also oligomers of TVS in whose PMR spectrum there are mainly the signals of the Me_3Si group while the signals with the corresponding intensity characteristic of methyl esters and acids were absent, were identified as by-products in the reaction mixture. The content of the by-products was 10-25% of the total identified compounds and dependent on the TVS concentration. The conditions for and the results of the GLC analysis in the analytical experiments, carried out similarly but in 5 ml ampules, are given in Table 2.

Addition of Methyl Bromoacetate to Trimethylvinylsilane. The experiments were carried out as described above. In the preparative experiments, 1.53 g of MBA, 0.3 g of TVS, and 0.12 g of PB were used. The mixture was heated for 5 h at 90°C. The yield of the adduct was ∿35% based on the charged telogen. The structure of the adduct (V) was confirmed by the data of PMR, ^{13}C NMR spectra, and elemental analysis. The conditions and the results of the GLC analysis in analytical experiments are given in Table 3. An aliquot portion of experimental mixture 1 (see Table 3) was heated again in the presence of $Mn_2(CO)_{10}$ at 140°C for 1 h; the content of the adduct did not change.

Addition of Methyl Bromoacetate to 1-Hexene. The experiments were carried out by the method described above. A mixture of 1.56 g of MBA, 0.056 g of 1-hexene, and 0.15 g of PB was heated for 3 h at 90°C. According to GLC, the conversion of MBA was ∿20%. The contents of the adduct and lactone (see Table 3) were respectively 5.1 and 4.6%, based on charged telogen. Lactone (VI) was isolated from the reaction mixture by preparative GLC. The adduct was not isolated as such, since under the preparative GLC conditions it converts into a lactone.

CONCLUSIONS

1. Radical telomerization of trimethylvinylsilane is similar to an analogous reaction of propylene, due to the similar influence of the Me_3Si and CH_3 groups on the neighboring radical center in the growing radical.

2. The telomerization of trimethylvinylsilane with methyl isobutyrate leads not only to the telomers with a normal structure, but also to the formation of an unsaturated compound $Me_3SiCH_2CH{=}CHCH_2CMe_2CO_2Me$.

3. In contrast to Fe(CO), decacarbonyldimanganese effectively initiates the addition of methyl bromoacetate to trimethylvinylsilane.

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A STUDY OF THE PRODUCTS FROM THE HETEROGENEOUS CATALYTIC OXIDATION OF MERCAPTAN

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When processing a mixture of hydrocarbons and organic sulfur compounds in the presence of oxygen a large number of various types of oxygen-containing sulfur compounds are formed as well as H_2S, SO_2, CO, and CO_2 [1, 2].

The problems of studying the mechanism of the catalytic conversion of sulfur compounds involve that of reliable identification of the reaction products which cannot be resolved without using modern physical and chemical methods of investigation.

In this investigation we have studied the products from the heterogeneous catalytic oxidation of ethyl mercaptan by NMR, GC, IR, and mass spectrometry.

EXPERIMENTAL

Ethyl mercaptan was passed over a mixed oxide catalyst at 200°C and a space velocity of 2000 h^{-1} in a mixture with methane and air. The reaction products formed were collected

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