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RADICAL REACTIONS OF 1,1-DIETHOXYMETHANE AND ETHYL FORMATE WITH TRIMETHYLVINYLSILANE

R. M. Makaeva, R. S. Musavirov,
E. A. Kantor, and A. B. Terent'ev

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Radical telomerization of ethylene with linear formals proceeds by cleavage of an α-C—H bond in an alkoxy group and leads to the formation of asymmetric formals [1]:

$$CH_2(OEt)_2 \xrightarrow{RO^\cdot} CH_2(OEt)O\dot{C}HMe \xrightarrow{nCH_2=CH_2} CH_2(OEt)OCH(Me)(CH_2CH_2)_nH \qquad (1)$$

In the present work, the radical addition of diethoxymethane (DEM) and ethyl formate to trimethylvinylsilane (TVS) initiated by tert-butyl peroxide (TBP) is investigated (Table 1). The use of unsaturated heteroorganic compounds as monomers is of interest both from the point of view of the synthesis of various carbofunctional compounds containing a C—heteroatom bond as well as from theoretical standpoints, since the nature of the monomer has a vital influence on the course of radical addition reactions and telomerization [2].

It could be expected that the reaction of TVS with DEM would proceed according to scheme (1) with the formation of the asymmetric formal (F), $CH_2(OEt)OCH(Me)CH_2CH_2SiMe_3$. However, preparative NMR (see Experimental section) showed that in the reaction mixture there is present only the silicon-substituted formate (T_a), formation of which can be shown by the following scheme:

$$\begin{gathered} CH_2(OEt)_2 \xrightarrow{RO^\cdot} CH_2(OEt)O\dot{C}HMe \xrightarrow{CH_2=CHSiMe_3} \underset{(A)}{CH_2(OEt)OCH(Me)CH_2\dot{C}HSiMe_3} \\ (A) \xrightarrow{1,5\text{-}H} \underset{(B)}{\dot{C}H(OEt)OCH(Me)CH_2CH_2SiMe_3} \\ (B) \xrightarrow{-Et^\cdot} \underset{(Ta)}{HC(O)OCH(Me)CH_2CH_2SiMe_3} \end{gathered} \qquad (2)$$

Until now, rearrangement of the type A → B for dialkoxymethanes has not been observed. An analogous rearrangement was studied previously for the case of the telomerization of ethylene with dimethoxyethane, where H migrates from the tertiary C atom in the radical $MeCH(OMe)\cdot OCH_2(CH_2CH_2)^\bullet_n$ [3].

Since ethyl formate is formed by radical conversions of the very same diethoxymethane, it is possible to present another pathway for formation of T_a:

$$\begin{gathered} HCO_2Et \xrightarrow{RO^\cdot} \left| \begin{array}{l} \to HCO_2\dot{C}HMe \\ \to \dot{C}O_2Et \end{array} \right. \\ HCO_2\dot{C}HMe + CH_2=CHSiMe_3 \to \underset{(C)}{HCO_2CH(Me)CH_2\dot{C}HSiMe_3} \xrightarrow{HD^*} T_a \end{gathered} \qquad (3)$$

Moreover, the isomeric compound T_b can also be formed in this reaction:

$$\dot{C}O_2Et + CH_2=CHSiMe_3 \xrightarrow{HD} \underset{(T_b)}{Me_3SiCH_2CH_2CO_2Et} \qquad (4)$$

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*HD = hydrogen donor.

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TABLE 1. Addition of 1,1-Diethoxymethane (DEM) to Trimethylvinylsilane (TVS) TBP 5%, 2 h

Experiment No.	Batch, mmole		Conversion, %		TVS/DEM initial	Yield of product based on reacted telogen, mole %		$\frac{\text{Ester } T_a}{\text{HCOOEt}}$, %
	TVS	DEM	TVS	DEM		HCOOEt	ester T_a	
1	0,5	10,6	82	9,8	0,05	55	Traces	–
2	1	11,3	96	10,5	0,09	52	Traces	–
3	2	13,8	94,8	12	0,14	40,5	6,3	16
4	5	14	91,3	9,7	0,36	47	11	25
5	4	10,8	76	7	0,37	62	13,3	22
6 [*]	2,7	9,3	32	11	0,29	–	1,2 (1,6)[†]	1–2[†]
7	7.1	9,9	80	6.7[‡]	0,70	77,6	15,5	24

[*] Telogen is ethyl formate.

[†] $Me_3SiCH_2CH_2COOEt$ ester, yield based on initial ethyl formate.

[‡] 70-80% of monomer oligomerizes.

To establish the possible routes of the reaction we studied also the radical addition of ethyl formate to TVS. In this reaction both adducts T_a and T_b are actually formed (schemes (3) and (4)) in similar proportions; the yield of each of them amounts to 1-2%, based on ethyl formate (Table 1, experiment 6).

In parallel experiments on the addition of diethoxymethane to TVS under comparable conditions the yield of adduct T_a (based on ethyl formate) amounts to more than 20% (experiments 4, 5), which is excluded by its formation according to Scheme (3).

By using GLC according to a previously established model the virtual absence of ester T_b in the reaction of diethoxymethane with TVS is shown, i.e., the rate of fragmentation of the radical $\dot{C}H(OEt)_2$ is considerably greater than its possible addition to TVS.

Apart from the compounds identified, oligomers of TVS are isolated, the content of which depends on the concentration of TVS (70-80% TVS is consumed in oligomerization).

It is interesting to note that under the conditions of the reaction of diethoxymethane with TVS, radical A (scheme (2)) isomerizes with 1,5-migration of H almost completely, not proceeding to any great extent to chain growth or transfer. This is evident from the absence in the reaction mixture of asymmetric formals of type F.

Such a high degree of rearrangement in this case can be explained in particular by an unfavorable combination of polar and steric factors for the competing reactions of chain transfer and growth.

Radical A has a relatively nucleophilic character; the same polar nature is also characteristic for the addition agent. Rearranged radicals B (scheme (2)) are slightly stabilized by fragmentation. This actually leads to a break in the kinetic chain, which explains the small yield of products calculated from the initiator taken into the reaction.

The reaction with ethyl formate (Table 1, experiment 6), where polar factors do not hinder the chain transfer stage, proceeds differently. In particular, the nucleophilic radical B (scheme (3)) undergoes chain transfer with the electrophilic ethyl formate, which leads to the formation of ester T_a.

In the ^{13}C NMR spectra of compounds T_a and T_b there are signals characteristic of carboxylic acid esters containing the Me_3Si group [4] in the chain and conforming to the structure proposed for these compounds. Classification of the signals is done in accordance with general rules studied previously [4] and on the basis of spectra recorded using the technique DEPT.

So as to establish the optimum conditions for obtaining T_a in the reaction of diethoxymethane with TVS the concentration of TBP was varied for TVS/DEM ratios of 0.1-0.3 (Table 2).

The figures in Table 2 show that even for 10% TBP and a TVS/DEM ratio of 0.3 (experiment 6) a fairly high conversion of DEM is achieved (20%) for a maximum content of T_a. For comparison, the yield of adduct is correlated (Table 2) with the yield of the first of the TVS oligomers identified.

The high conversion of monomer results in the fact that an increase in reaction time (more than 1 h) has virtually no effect on the yield of adduct. By changing the reaction time from 0.5 to 2.5 h (at 135°C) the content of adduct (based on reacted diethoxymethane) increases slightly (Experimental section).

TABLE 2. Effect of TBP Concentration and TVS/DEM on the Yield of Adduct T_a

Experiment No.	TVS/DEM, initial	TBP, %	Conversion, %		Content of products based on reacted telogen, %		Adduct
			TVS	DEM	adduct	TVS oligomer*	TVS oligomer*
1	0,1	5	95	11	Traces	Traces	–
2	0,2	5	95	12	9,5	2	4,7
3	0,3	5	90	6	10,5	4,5	2,3
4	0,1	10	100	12	10,8	4,5	2,4
5	0,2	10	100	21	9,4	3,1	3,0
6	0,3	10	100	19	13,8	6,1	2,3
7	0,1	20	100	23	2,0	0,7	2,9
8	0,2	20	100	22	9,1	3,8	2,4
9	0,3	20	100	22	10,9	4,5	2,4

*The first of the identified oligomers is taken for the calculation.

EXPERIMENTAL

^{13}C NMR spectra were recorded on a Bruker WP-200 spectrometer (internal standard CCl_4); PMR spectra were recorded on a Perkin–Elmer R-20 spectrometer, GLC analysis was carried out on a LKM-80 chromatograph, column 3 × 2000 mm with 15% SE-301 on Chromaton N-AW, katharometer, helium. Preparative GLC: column 9 × 1300 mm with 20% SKTFT on Chromaton N-AW.

Addition of 1,1-Diethoxymethane to Trimethylvinylsilane. Preparative experiments were conducted in sealed glass ampuls (30 ml) previously evacuated and filled with nitrogen. The ampuls with the starting compounds (12.1 g diethoxymethane, 2.1 g TVS, and 0.6 g TBP) were placed in metal holders and heated on an oil bath for 2 h at 140°C with mixing by rotation. The reaction mixture from the six experiments was combined and the starting compounds distilled off. The residue (16 g, 22% based on diethoxymethane) was fractionated under vacuum. From the fraction with bp 65-85°C (10 mm) (1.4 g) the formate $HC(O)OCH(Me)CH_2CH_2SiMe_3$, n_D^{20} 1.4194, d_4^{20} 0.8720, was separated by preparative GLC. PMR spectrum (δ, ppm from TMS): 8.3 s (HCOO), 5.0 m (OCH), 1.4 t (CH_2), 1.2 d (CH_3), 0.4 m (CH_2Si), –0.1 s ($Si(CH_3)_3$). ^{13}C NMR spectrum (δ, ppm from TMS): 159.1 (HCOO), 72.0 (OCH), 30.0 (CH_2), 19.2 (CH_3), 11.8 (CH_2Si), –1.9 (Me_3Si). Found, %: C 55.53; H 10.54; Si 16.35. $C_8H_{18}O_2Si$. Calculated, %: C 55.17; H 10.34; Si 16.09. TVS oligomers were separated as byproducts; their PMR spectra have signals only upfield at 0.1-1.2 ppm. Found, %: C 60.32; H 13.36; Si 24.03. $C_8H_{18}O_2Si$. Calculated, %: C 55.17; H 10.34; Si 16.09. TVS oligomers were separated as byproducts; their PMR spectra have signals only upfield at 0.1-1.2 ppm. Found, %: C 60.32; H 13.36; Si 24.03. $C_5H_{14}Si$. Calculated, %: C 60.0; H 12.0; Si 28.0. The conditions and results of the GLC analysis of the analytical experiments conducted similarly but in ampuls of capacity 5 ml are given in Tables 1 and 2. 70-80% TVS is consumed in oligomerization. The content of formate T_a (based on reacted diethoxymethane) on changing the reaction time (TBP = 5%, 135°C, TVS/DEM = 0.3) is given below (standard – $CH_2(CO_2Me)_2$).

τ, h	0,5	1,0	1,5	2,0	2,5
$[T_a]$, %	8,4	11,1	11,3	13,0	12,7

Addition of Ethyl Formate to Trimethylvinylsilane. The experiments were conducted similarly to those described above. In the preparative experiments 13 g ethyl formate, 4 g TVS, and 0.7 g TBP were taken. Five preparative experiments were carried out. From the fraction with bp 30-45°C (2 mm) (1.3 g) were separated two adducts, $HCOOCH(Me)CH_2CH_2SiMe_3$ (details given above) and $Me_3Si(CH_2)_2CO_2Et$. ^{13}C NMR spectrum (δ, ppm from TMS): 172.8 (CO_2), 59.3 (CH_2O), 28.4 (CH_2), 14.2 (CH_3), 11.3 (CH_2Si), –1.9 ($Si(CH_3)_3$). PMR spectrum (δ, ppm from TMS): 4.00 q (OCH_2), 2.24 m (CH_2), 1.2 t (CH_3), 0.7 m (CH_2Si), –0.1 ($Si(CH_3)_3$). Found, %: C 55.46; H 10.50; Si 14.85. $C_8H_{18}O_2Si$. Calculated, %: C 55.17; H 10.34; Si 16.09.

CONCLUSIONS

1. In the radical reaction of 1,1-diethoxymethane with trimethylvinylsilane the silicon-containing formate $HC(O)OCH(Me)(CH_2)_2SiMe_3$ is formed by rearrangement of the radical $CH_2(OEt)OCH(Me)CH_2\dot{C}HSiMe_3$ with 1,5-migration of an H atom and subsequent fragmentation.

2. The addition of ethyl formate to trimethylvinylsilane proceeds both by acyl and by alkoxyl groups and gives the adducts $Me_3Si(CH_2)_2COOEt$ and $HCOOCH(Me)(CH_2)_2SiMe_3$.

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HOMOLYTIC ADDITION OF 2-ETHOXY-1,3-DIOXOLANE TO 1-DECENE

I. I. Khatuntsev, E. V. Pastushenko,
D. É. Kruglov, and A. B. Terent'ev

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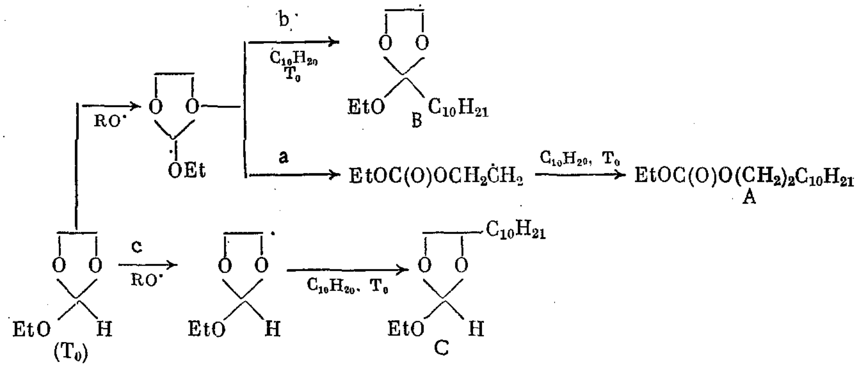
Radical addition of ethyl orthoformate to α-olefins leads to the formation of the adduct-carbonate $EtOC(O)OCH(Me)C_nH_{2n+1}$ (I) [1, 2]. The analogous carbonates are obtained in the process of telomerization of ethylene with diethylcarbonate [3]

$$\underset{(T_0)}{(EtO)_2CO} + nCH_2{=}CH_2 \xrightarrow[T_0]{RO^\cdot} \underset{(T_n)}{EtOC(O)OCH(Me)(CH_2CH_2)_nH} \qquad (1)$$

The structure of the compounds (I), n = 3, 4, and T_n, n = 1-4, is confirmed by data from ^1H and ^{13}C NMR spectroscopy. In this report the radical addition of the cyclic orthoester 2-ethoxy-1,3-dioxolane to 1-decene was studied. In this case the formation of a series of cyclic compounds can be expected. Moreover, adducts of linear structure can form due to the ring-opening reactions that are characteristic of compounds of this type (Scheme 1).

Scheme 1



Due to the complex composition of the reaction mixture and the thermal instability of the cyclic orthoester under the conditions of preparatory gas—liquid chromatography, the reaction is studied using the method of chromato-mass spectrometry. The mass spectra of two adduct-carbonates (Table 1, Nos. 1, 2) [1, 3] and 2-ethoxy-1,3-dioxolane (No. 3) were recorded to show the mass spectral characteristics of the adducts with cyclic and linear structure. The more intense peaks in the spectra of the carbonates were m/z 45 $[EtO]^+$, 140 $[C_{10}H_{20}]^+$ (No. 1), or 168 $[C_{12}H_{24}]^+$ (No. 2) depending on the length of the hydrocarbon chain of the alkyl group (Scheme 2a). The peaks with m/z 73 $[CH(OCH_2)_2]^+$ and to a lesser degree 45 $[EtO]^+$ are the

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