CONCLUSIONS

1. Alkylthiodiorganoboranes add at the $C\equiv N$ bond of phenylacetonitrile under mild conditions to form diorganoboryl derivatives of the respective S-alkylthioimidates.

2. By means of the reaction of phenylacetonitrile with alkylthiodiorganoboranes (in 2:1 ratio), chelate compounds of boron were synthesized with the respective deprotonated β-iminothioimidates as ligands.

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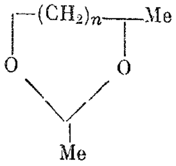
RADICAL TELOMERIZATION OF VINYLTRIMETHYLSILANE WITH SUBSTITUTED 1,3-DIOXANES

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

UDC 541.515:66.095.2:547.345:547.841

The radical reaction of vinyltrimethylsilane (VTMS) with 2-methyl-1,3-dioxolane proceeds with the formation of compounds of both cyclic and linear structure; the latter are formed as a result of ring opening in a radical intermediate [1]. A study of the homolytic conversion of 2,4-dimethyl-1,3-dioxacyclanes showed that ring opening occurred to the greatest extent at the most substituted carbon atom [2]



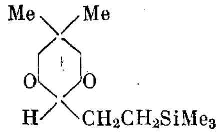
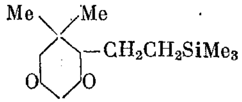
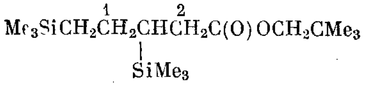
n = 0, 1, 2.

Radical reactions of VTMS with 1,3-dioxanes has not previously been described.

With the object of clarifying the effect of ring size, and the number and position of the substituents in the dioxane, on the direction of the radical addition and telomerization with VTMS, we have studied the radical telomerization of VTMS with 4-methyl-1,3-dioxane (MD) and 5,5-dimethyl-1,3-dioxane (DMD).

A. N. Nesmeyanov Institute for Organometallic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2092-2097, September, 1986. Original article submitted April 26, 1985.

TABLE 1. Carbon-13 and Proton Spectra and Physicochemical Constants of Identified Compounds

Compound	Spectrum	δ, ppm: OCH(P)O, OCH₂O, C(O)O	δ, ppm: CH₂O, CHO	δ, ppm: $-\overset{\vert}{\underset{\vert}{C}}-$	δ, ppm: Me	δ, ppm: MeSi, CH₂Si, CHSi	δ, ppm: CH, CH₂	n_D^{20} / d_4^{20}	Calculated/Found, %: C	Calculated/Found, %: H	Calculated/Found, %: Si
 (I)	^{13}C	103,3	76,7	29,9	21,9 23,1	−1,7 10,0	28,9	1,4390 / —	61,05 / 61,40	11,18* / 11,39	
	^1H	4,26 t (1H)	3,41 m (4H) †	—	0,68 s (3H), 1,14 s (3H)	−0,01 s (9H) 0,52 m (2H)	1,53 m (2H)				
 (II)	^{13}C	93,9	78,1 87,3	33,4	18,5 21,9	−1,6, 12,9	23,1				
	^1H	4,79 q (2H)	3,35 m (2H) † 3,02 m (1H) †	—	0,70 s (3H) 1,03 s (3H)	−0,01 s (9H) 0,34 m (2H)	1,35 m (2H)				
$HC(O)OCH_2C(Me_3)_2\overset{1}{C}H_2\overset{2}{C}H_2CH_2SiMe_3$ (III)	^{13}C	159,2	70,9	33,7	24,2	−1,6 17,4	17,9 (2) 43,2 (1)				
	^1H	8,0 s (1H)	3,85 s (2H)	—	0,9 s (6H)	−0,1 s (9H) 0,45 m (2H)	0,7−1,25 m (1,2)				
 $Mr_3SiCH_2\overset{1}{C}H_2\underset{\vert \atop SiMe_3}{C}H\overset{2}{C}H_2C(O)OCH_2CMe_3$ (IV)	^{13}C	172,4	72,9	31,2	26,6	−1,8 ÷ −2,3 15,5 25,4 (CH)	23,9 (1) 33,8 (2)	1,4452 / —	60,69 / 60,95	11,46 / 11,38	17,74 / 16,70
	^1H	—	3,69 s (2H)	—	0,93 s (9H)	−0,02 s (9H), −0,03 s (9H), 1,09 m (1H) 0,49 m (2H)	1,39 m (2H) (1) 2,24 d (2H) (2)				
$HC(O)O\overset{1}{C}H_2CH_2CH(Me)\overset{2}{C}H_2CH_2SiMe_3$ (V)	^{13}C	159,6	61,6	—	18,9	−1,8; 13,2	32,4, 34,8 (1), 30,8 (2)	1,4337 / 0,8732	59,35 / 59,68	10,96 / 11,16	13,88 / 14,79
	^1H	8,84 s (1H)	4,61 t (2H)	—	0,93 d (3H)	−0,02 s (9H) 0,48 m (2H)	1,08−1,84 s				
$HC(O)O\overset{1}{C}H_2CH_2C(Me)(\overset{2}{C}H_2CH_2SiMe_3)^2$ (VI)	^{13}C	159,2	60,2	35,5	21,0	−1,8; 9,3	32,5 (2) 35,9 (1)	1,4490 / 0,8672	59,54 / 60,24	11,33 / 11,68	18,56 / 19,66
	^1H	7,68 s (1H)	4,13 t (2H)	—	0,82 s (3H)	−0,02 s (9H) −0,03 s (9H) 0,39 m (2H)	1,55 s (2H) (1), 1,17 m (2H) (2)				

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*Elemental analysis carried out on a mixture of isomers of (I)-(III).

†AB quadruplet.

TABLE 2. Radical Telomerization of Vinyltrimethylsilane (VTMS) with 5,5-Dimethyl-1,3-dioxane (DMD) [140°C, 2 h, 1% $(t\text{-}BuO)_2$]

Charge, mmole		Conversion, %		Composition of aggregate of identified telomers, mole %			
VTMS	DMD	VTMS	DMD	(I)	(II)	(III)	(IV)
0,7	14,2	98	3	49	14	17	20
1,4	13,7	93	9	44	17	12	27
2,4*	11,8	99	12	46	18	15	21
2,7*	9,1	92	4	38	19	12	31

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*5% $(t\text{-}BuO)_2$.

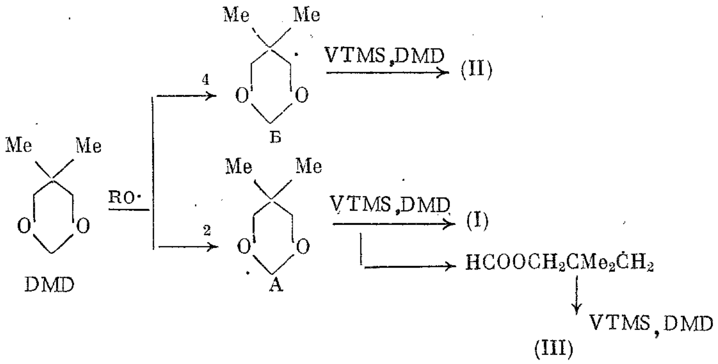
TABLE 3. Radical Telomerization of Vinyltrimethylsilane (VTMS) with 4-methyl-1,3-dioxane (MD) [140°C, 2 h, 5%$(t\text{-}BuO)_2$]

Charge, mmole		Conversion of MD *, %	Composition of aggregate of identified telomers, mole %†			
VTMS	MD		$HC(O)OC_4H_9$	(V)	(VI)	Maxima
0,4	7,2	2	71,2	19,2	6,4	3,2
0,6	6,2	10	63,3	17,4	5,5	13,8
1,4	7,0	9	45,3	29,7	14,0	11,0
1,6	5,2	11	21,2	35,9	19,5	23,3
2,5	6,2	10	16,4	17,6	13,9	52,9

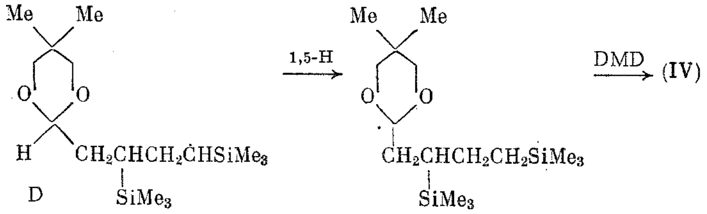
*Conversion of VTMS = 80-90%.

†The concentration of products in the reaction mixture from GLC results (internal standard dimethyl malonate) = 4.5 to 5% (45-50% on reacted MD).

The telomerization of VTMS with DMD in the presence of $(t\text{-}BuO)_2$ leads to a combination of linear and cyclic structures with a single monomeric unit: $OCH_2C(Me)_2CH_2OCHCH_2SiMe$ (I), $OCH_2OCH_2C(Me)_2CHCH_2CH_2SiMe_3$ (II), $HCOOCH_2C(Me)_2CH_2CH_2CH_2SiMe_3$ (III), and a linear telomer with two monomeric units, $Me_3SiCH_2CH_2CH(SiMe_3)CH_2COOCH_2CMe_3$ (IV). Adducts (I) and (III) are formed by substitution into the DMD in positions 2 and 4 in the ring and adduct (III) by ring-opening of the cyclic radical A



It seems that, in the course of the formation of the telomer (IV), a 1,5-transfer of hydrogen takes place in the cyclic radical D with two monomeric units with subsequent opening of the ring and chain transfer to DMD



Compounds (I)-(IV) were isolated in pure form and their structure confirmed by carbon-13 and proton NMR (Table 1). The methyl groups in (I) and (II) are nonequivalent and appear in the carbon-13 spectrum as two signals separated by 1-3 ppm. A similar picture is observed in the proton spectrum where the chemical shifts of the protons of these groups are separated by 0.46 ppm for (I) and 0.33 ppm for (II). The same nonequivalence is apparently connected with the existence of a preferred conformation of the six-membered ring.

The formate (III) is characterized in the carbon-13 spectrum by signals for carbon atoms in the HCOO, CH_2O, and CMe_3 groups; two equivalent groups in them are represented by one signal at 24.2 ppm. All the compounds have characteristic signals for the Me_3Si groups (−1.6, −2.3 ppm) and CH_2Si (10-12 ppm).

Only one telomer with two monomer units [compound (IV)] was isolated from the reaction mixture; its carbon-13 spectrum showed signals for C(O)O (172.4 ppm), CH_2O (72.9 ppm), CH_2Si (15.5 ppm), and CHSi (25.4 ppm). The combination of the two latter signals is characteristic for telomers with two monomer units. It is possible that the remaining telomers of this group are formed, but in considerably smaller amounts.

Position 2 in 1,3-dioxane naturally is the most reactive, and this also determines the preferential formation of compounds (I) and (II) (Table 2). The formate (III), arising as a result of initial ring-opening of radical A, can also be ascribed to this. The considerably greater yield, under the present reaction conditions, of the adduct with cyclic structure (I) should also be noted in comparison with the linear adduct (III).

The studied reaction is one of a few examples where the reaction is recorded at position 4 of the ring. During an ESR study of the direction of the reaction of different radicals with 1,3-dioxacyclanes, it was shown that detachment of hydrogen took place preferentially at position 2 of the ring and radicals were formed only to a small extent as a result of detachment of hydrogen at position 4.

The telomerization of VTMS with 4-methyl-1,3-dioxane proceeds more unequivocally and leads to telomers which do not incorporate a dioxane ring: $HCOOCH_2CH_2CH(Me)CH_2CH_2SiMe_3$ (V) and $HCOOCH_2CH_2C(Me)(CH_2CH_2SiMe_3)_2$ (VI) (Table 3). The structure of (V) was confirmed by the results of the carbon-13 spectrum which contained characteristic signals analogous to those for compound (III). The presence of a signal for CH_2O in the spectrum, and the absence of a signal for $CH_3{}^{13}CHO$ indicates that ring-opening in radical E occurs solely at a C—O bond at the most substituted carbon atom of the ring.

According to the carbon-13 spectrum, compound (VI) (see Table 1) contains two identical $CH_2CH_2SiMe_3$ groups (signals of doubled intensity), and hence we proposed a rearrangement of the intermediate radical with 1,3-migration of a hydrogen atom

$$\begin{gathered}HCOOCH_2CH_2CH(Me)CH_2\dot{C}HSiMe_3 \xrightarrow{1,3\text{-}H}\\ \rightarrow HCOOCH_2CH_2\dot{C}(Me)CH_2CH_2SiMe_3 \xrightarrow{VTMS,\ DN} \text{(VI)}\end{gathered}$$

Compound (VI), according to GLC results and its carbon-13 spectrum, is the most abundant (80-90%) among telomers with two monomer units.

The data in Table 3 indicate that the fraction of higher telomers increases with increase in monomer concentration and that radical addition of 5,5-dimethyl-1,3-dioxane to VTMS proceeds largely with retention of the dioxane ring of the telogen. Introduction of a substituent into position 4 of the 1,3-dioxane significantly changes the route of the process: the dioxane ring of the telogen is opened with selective breaking of the C—O bond at the most-substituted carbon atom.

EXPERIMENTAL

Carbon-13 NMR spectra were obtained on a Bruker WP-200 spectrometer using CCl_4 as internal standard. GLC was effected on an LKhM-80 chromatograph programmed from 100°C at 4 deg/min with a 3000 × 3 mm stainless steel column packed with 15% SKTFT-50 on chromatone N-AW-HMDS with helium carrier gas.

Radical Telomerization of Vinyltrimethylsilane with 5,5-Dimethyl-1,3-dioxane. a) Preparative experiments were carried out in sealed glass ampuls of 30-ml capacity, previously evacuated and filled with nitrogen. The ampuls with the starting materials [11 g DMD, 1.9 g VTMS, and 0.5 g $(t\text{-}BuO)_2$] were placed in metal cases and rotated while heating in an oil bath at 140°C for 2 h. Six preparative experiments were carried out and the reaction products combined and the starting materials distilled out. The reaction product (14.6 g) was fractionated in vacuo. From the fraction with bp 70-100°C at 3 mm (2.4 g) the following products were separated by preparative GLC (number, yield in g; from GLC results): (I), 1.1; (II), 0.5; (III), 0.5. From the fraction with bp 100-140°C at 3 mm (1.6 d), 1 g compound (IV) was isolated.

b) Analytical experiments were carried out in a similar way in ampuls of 4-ml capacity. The results are set out in Table 2.

Radical Telomerization of Vinyltrimethylsilane with 4-Methyl-1,3-dioxane. a) Preparative experiments were carried out using the method described above. For each experiment, 11 g MD, 3.2 g VTMS, and 0.6 g $(t\text{-}BuO)_2$ were taken. Six experiments were carried out. From the fraction with bp 50-65°C at 1 mm (2.8 g), 1.7 g compound (V) (from GLC results) was isolated by preparative GLC. From the fraction with bp 65-110°C at 1 mm (2.8 g), 1.2 g compound (VI) was isolated. Dimethyl malonate was used as an internal standard.

b) The results of the analytical experiments are shown in Table 3.

The results of the carbon-13 and proton NMR examinations, elemental analyses, and physicochemical constants are shown in Table 1.

CONCLUSIONS

1. Radical telomerization of vinyltrimethylsilane with 5,5-dimethyl-1,3-dioxane leads in the main to retention of the dioxane ring of the telogen and its substitution in positions 2 and 4.

2. When 4-methyl-1,3-dioxane is used in the telomerization of vinyltrimethylsilane, the course of the reaction is changed; the dioxane ring of the telogen is generally opened with regioselective breaking of a bond at the most-substituted carbon atom.

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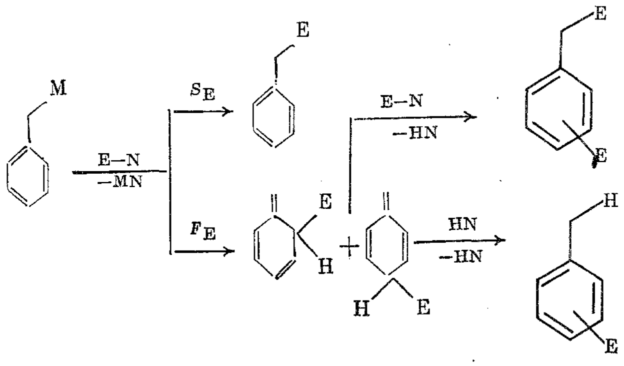
ACETYLDEMETALLATION OF BENZYLTRIMETHYLSTANNANE IN THE PRESENCE OF ALUMINUM BROMIDE

V. I. Rozenberg, V. A. Nikanorov,
and O. A. Reutov

UDC 542.97:547.258.11:546.623'141

A characteristic property of organometallic benzyl compounds in reactions with electrophiles is the possibility of concurrent attacks at the α-C atom (electrophilic substitution, S_E) and at the o- or p-position of the benzene ring to form intermediate semiquinone structures (electrophilic fragmentation, F_E):



We have previously expressed the supposition that the reaction with attack on the benzene ring, when benzyl derivatives of Hg react with CH_3COCl in the presence of $AlBr_3$ [1], can be considered as heterolytic fragmentation (F_E) [2]. The present work studies the possibility of analogous reactions for the Sn analog $PhCH_2SnMe_3$. The latter does not react with a tenfold excess of MeCOCl either in CH_2Cl_2 (42°C, 2-4 days) or in a sealed ampul (60°C, 1.5 days). But, in the presence of $AlBr_3$ (cf. [3]) in an argon atmosphere this reaction goes smoothly even at reduced temperature:*

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*It is impossible to ignore the possibility of acetyldestannation of $PhCH_2SnMe_3$ via scission of the Me—Sn bond. Indeed, at −20° the reaction forms 5% acetone. Therefore, subsequently

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2097-2101, September, 1986. Original article submitted April 6, 1985.