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LINEAR CO-OLIGOMERIZATION OF VINYLSILANES WITH BUTADIENE AS A METHOD OF SYNTHESIZING SILICON-CONTAINING POLYENES

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Summary

The linear co-oligomerization of trimethylvinylsilane with butadiene takes place on a nickel-containing catalytic system with formation of 1-trimethylsilyl-*trans,trans*- and 1-trimethylsilyl-*cis,trans*-deca-1,4,9-trienes. Desilylation of the resultant trienes with $MoCl_5$ leads to the known compound deca-1,4,9-triene. Hydroalumination of decatrienylsilanes with diisobutylaluminium hydride and subsequent hydrolysis yield 1-trimethylsilyl-*trans*-deca-4,9-diene and 1-trimethylsilyl-*trans*-dec-4-ene. The interaction of butadiene with trimethoxyvinylsilane occurs more selectively to form only 1-trimethoxysilyl-*cis,trans*-deca-1,4,9-triene. A suitable scheme is suggested on the basis of the structure of butadiene-d_6-trimethylvinylsilane co-oligomerization products.

Introduction

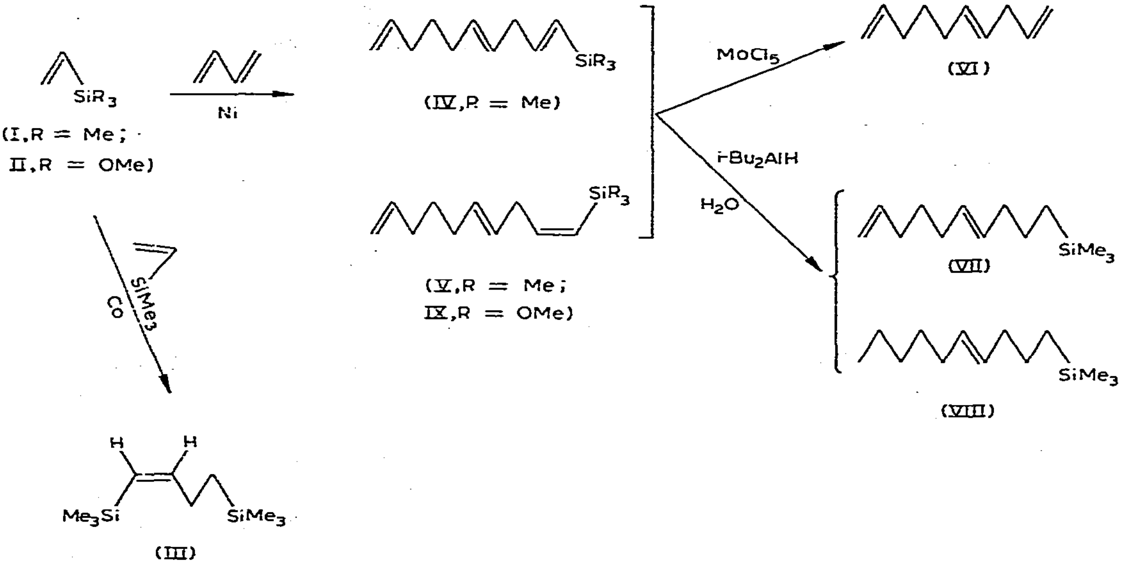
As is known from the literature [1—6], one of the most suitable methods for obtaining silicon-containing olefins is by polyene hydrosilylation involving catalysis by complexes of platinum, palladium, rhodium, nickel, cobalt and other transition metals. We have developed a new way of synthesizing silylated polyenes based on the linear co-oligomerization of vinylsilanes with 1,3-dienes, catalyzed by nickel complexes. Co-oligomerization reactions of simple monoolefins with 1,3-dienes have been studied adequately. These reactions served as a basis for developing the synthesis of decatrienes, including those containing functional groups [7—11].

Results and discussion

The present communication deals with a study of the co-oligomerization of butadiene with vinyltrimethyl- (I) and vinyltrimethoxy-(II)-silanes.

Since the formation of homo-oligomers is to be expected during co-oligomerization, experiments with vinylsilane I were carried out in order to identify the homo-oligomers. In the presence of a catalytic system comprising cobalt oxyquinolate, triphenylphosphine (TPP) and triethylaluminium (TEA), in the molar ratio $2/7 \times 10^{-3}/7 \times 10^{-3}/5 \times 10^{-2}$, vinyl silane I was found to form 1,4-bis(trimethylsilyl)but-1-ene (III) on heating to 100°C for 10 h, the yield being 30% and the monomer conversion 45%. The same product III was also formed when nickel acetylacetonate [Ni(acac)$_2$] was used, but with lower yield (Scheme 1).

SCHEME I



In a catalytic system comprising Ni(acac)$_2$, TPP and TEA (molar ratio 2/1/ $4 \times 10^{-3}/4 \times 10^{-3}/2 \times 10^{-2}$), butadiene and trimethylvinylsilane, upon heating to 100°C for 10 h, yield a 72% mixture of silyldecatrienes IV and V, ratio 1/1. Varying the molar ratios of butadiene and trimethylvinylsilane does not affect the composition of the reaction products. Moreover, neither cyclic co-oligomerization products nor linear and/or cyclic dimers of the initial reagents were detected in the reaction mixture.

Both 1-trimethylsilyl-*trans,trans*-(IV) and 1-trimethylsilyl-*cis,trans*-(V)-deca-1,4,9-trienes were isolated individually by preparative gas-liquid chromatography (GLC). The PMR spectra of silanes IV and V were virtually identical. The signals of the methyl protons attached to the silicon atom occur to high field (δ 0.12 and 0.13 ppm). Multiplets centred at δ 1.40 and 1.37 ppm correspond to the C^7 methylene protons. The C^6 and C^8 protons resonate as a multiplet centred at δ 2.00 ppm, while the C^3 protons resonate to low field (δ 2.45—2.70 ppm). The double bond proton signals are overlapped and hence are difficult to assign (multiplet at 4.60—6.20 ppm with integral corresponding to seven protons).

The ultra-violet spectra of silanes IV and V lack absorption bands at 230—240 nm characteristic of conjugated diene systems. The infrared spectra of these products are only distinguishable in the range of asymmetrical bending vibrations of C—H with a double bond. Thus, in the spectrum of V there is an intense absorption band at 780 cm^{-1} which is absent in the spectrum of IV. A common feature of both spectra is the presence of absorption frequencies at 915, 975, 1000, 1605, 1650, 3020 and 2080 cm^{-1}, this being characteristic of end vinyl groups, and disubstituted double bonds. It is noteworthy that the displacement of one of the absorption bands in the stretching vibrations of the C=C-group to 1605 cm^{-1} is ostensibly due to the effect of the silyl substituent.

Among the experiments to confirm the structure and stereochemistry of the oligomers, disilylation of silane V by molybdenum pentachloride appears to be the most interesting. This reagent proved efficient in desilylation processes involving aryl- and alkyl-silanes [12]. As a result, the known compound *trans*-deca-1,4,9-triene (VI) [7,8] gave a 40% yield: this product was also obtained on desilylating IV. The formation of the same triene VI from IV and V confirms unambiguously that silanes IV and V differ from each other only in the geometry of the double bond at the silicon atom (Δ^1), the configurations in IV and V being *trans* and *cis*, respectively. (In the IR spectrum of VI, the absorption bands at 780 and 1605 cm^{-1} disappear.)

The IR spectrum of triene VI differs from that of the initial silane V in that it lacks absorption bands at 700, 850—870 and 1250 cm^{-1} due to C—$Si(CH_3)_3$, and also at 780 and 1605 cm^{-1}. Hence it is possible to assign *trans* and *cis* configurations to Δ^4 and Δ^1, respectively of the double bond in V.

Investigation of the hydroalumination of IV and V with diisobutylaluminium hydride (DIBAH) showed that these compounds can react along both the end vinyl and the Δ^1-disubstituted double bonds. Hydrolysis of the hydroalumination products resulted in a mixture containing 1-trimethylsilyl-*trans*-deca-4,9-diene (VII) and 1-trimethylsilyl-*trans*-dec-4-ene (VIII), 1/1. These compounds were isolated in the pure state with the aid of preparative GLC. A point of note was the high reactivity of the double bond at the silicon atom, a phenomenon observed recently while studying silicon-containing diene cyclization in the presence of DIBAH [13].

Unlike trimethylvinylsilane, trimethoxyvinylsilane reacts with butadiene to form a single product, 1-trimethoxysilyl-*cis,trans*-deca-1,4,9-triene (IX). The ^{13}C NMR spectrum of this product (see Fig. 1) has eleven separate lines, thus excluding symmetrically situated double bonds. The triplet and doublet signals at 114.4 and 138.0 ppm are assigned to C^9 and C^{10} (end vinyl group). The signal at 150.9 ppm is unusual for a C=C double bond and is due to the situation of the bond in an α-position with respect to the electron-acceptor group $Si(OCH_3)_3$. Due to the I-effect of this group and the strong d_π—p_π interaction [14], the signal of the β-olefin carbon atom, C^2, is shifted to low field. The fact that C^3 is situated between two double bonds also causes its signal to be displaced to low field. A calculation performed in accordance with Dorman et al. [15] made it possible to assign the signals at 28.8, 32.0 and 33.3 ppm to C^7, C^6 and C^8, respectively.

The structure of IX is in agreement with the mass spectra for the negative ions of dissociative electron capture (NIDEC) shown in Table 1. This method was used earlier to establish the structures of some polyenes [16] and alkenyltrialkylsilanes [17]. The regularities deduced for ion disintegration channels

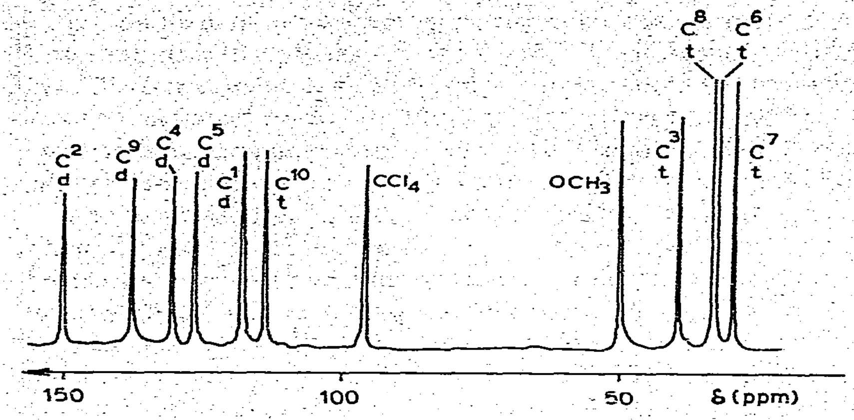
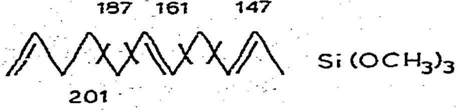


Fig. 1. ^{13}C NMR spectra for 1-trimethoxysilyl-*cis,trans*-deca-1,4,9-triene (IX).

were used to establish the location of the double bonds in IX. As is apparent from Table 1, the presence in the spectrum of ion lines of *m/e* 201, 187, 161 and 147 is indicative of a cleavage in the C—C σ-bonds of the alkenyl substituent in the product studied:



Furthermore, the NIDEC mass spectrum contains several ion lines that cannot

TABLE 1

MASS SPECTRA OF NEGATIVE IONS OF DISSOCIATIVE ELECTRON CAPTURE FROM 1-TRIMETHOXYSILYL-*cis,trans*-DECA-1,4,9-TRIENE (IX) AND TRIMETHOXYVINYLSILANE (II)

Compound IX		Compound II	
m/e	Relative intensity (%)	*m/e*	Relative intensity (%)
255	100	147	1.9
223	31.5	146	3
201	22	145	21.3
187	11.5	135	2.5
161	10	134	1.75
147	13	133	8.8
145	2	131	1.2
135	8.5	121	15
134	1.8	117	25
121	20	115	2
109	2.8	75	9
107	5	31	100
75	1	27	12
55	11.5	25	0.5
31	33	15	1.5
15	3		

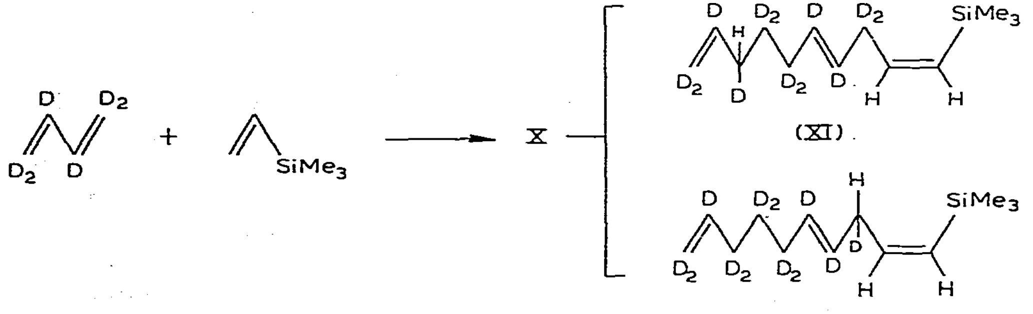
be explained solely by the above-mentioned cleavage of C=C σ bonds. The presence of these lines is associated with the R—CH=CH—Si(OCH$_3$)$_3$ group. To prove this a trimethoxyvinylsilane spectrum was recorded (Table 1): the mass spectrum of trimethoxyvinylsilane contained the same ion lines as those in IX, which indicates that similar disintegration channels exist for the trimethoxyvinylsilane fragments of both compounds.

The ^{13}C NMR and NIDEC spectra are in agreement with ozonization results. After diazomethane methylation of the acids obtained on ozonolysis of IX, GLC was used to establish the presence of the dimethyl esters of malonic and glutaric acids.

All the above data permits the double bonds in the alkenyl substituent of IX to be assigned to C^1, C^4 and C^9.

To explain our proposed scheme for the process of co-oligomerization, we examined the interaction of butadiene-d_6 with trimethylvinylsilane. The reaction was carried out at 105°C for 14 h. The yield of decatriene derivatives was as high as 45%. The main product X (ca. 52%) was isolated by preparative GLC. According to the mass spectra, the deuterized decatrienylsilane X has *m/e* 220. The bending vibrations in the IR spectrum of the —HC=CH— bond contained absorption frequencies at 730, 910 and 1000 cm^{-1}; only one band at 1605 cm^{-1} was present in the region of stretching vibrations. The displacement of one of the absorption bands (1650 cm^{-1}) to 1600 cm^{-1} was apparently due to the influence of the deuterium atoms at C^4, C^5, C^9 and C^{10}. The trimethylsilyl fragment had the same effect.

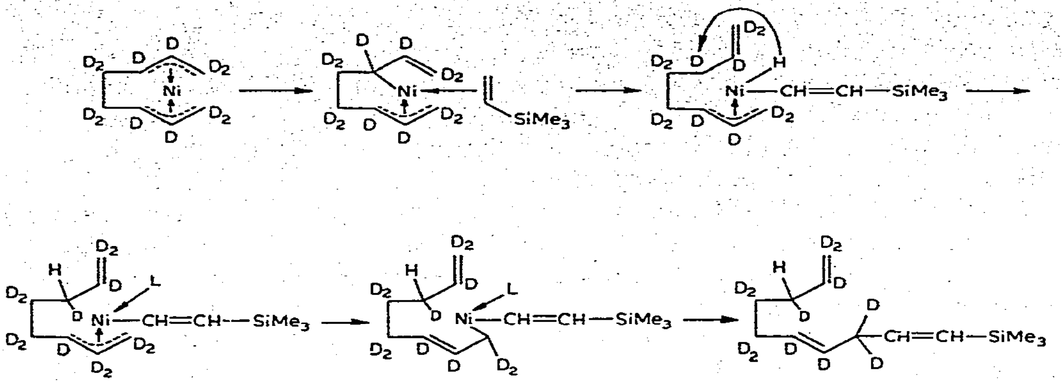
The PMR spectrum of the deuterized product X contains a triplet and doublet at 5.91 and 5.62 ppm, respectively, a doublet and singlet at 2.68 and 1.93 ppm, respectively, and proton signals of the silyl methyl groups at —0.02 and —0.03 ppm, respectively. Interpretation of the spectrum, taking into account the integral curve, and the signal resonance regions and their nature indicates that X represents a 1/1 mixture of isomers of 3,3,4,5,6,6,7,7,8,9,10,10-dodecadeutero-(XI)- and 3,4,5,6,6,7,7,8,8,9,10,10-dodecadeutero-(XII)-*cis,trans*-deca-1,4,9-trienyltrimethylsilanes, (eq. 1.)



(XII)

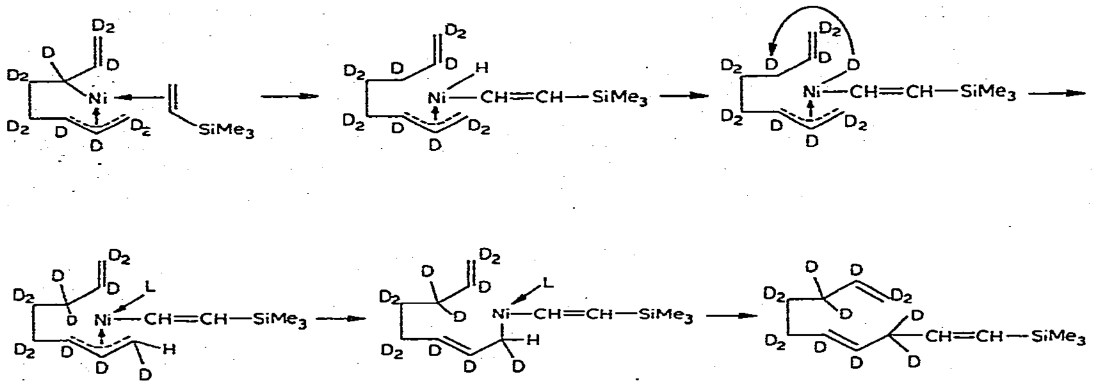
(1)

It is apparent from eq. 2 and 3, that formation of the oligomer XI is quite conceivable by using the widely known interpretations of Wilke et al. [7,8]. It is more difficult, however, to explain the existence of the second isomer XII containing a proton at C^3. Possibly, the exchange of deuterium for hydrogen occurs in the π-allyl complex.



(XI)

(2)



(XII)

(3)

Experimental

IR and UV spectra were recorded on UR-20 spectrophotometers (as films) and SPECORD UVvis instruments (alcohol solutions). PMR spectra were recorded on a Tesla BS-487B instrument as solutions in CCl_4 (operating frequency 80 MHz) without and with proton stabilization with respect to HMDS. The ^{13}C NMR spectrum was obtained on a Bruker WH-90 spectrometer at 22.63 MHz with wide-band suppression along the protons and in monoresonance mode. The chemical shifts are cited in ppm (δ scale for trimethylsilane) using a CCl_4 (96.0 ppm) signal as the internal standard. Mass spectra were recorded on a MX-13-03 spectrometer (electron ionization energy 50 eV, ionization temperature 200°C). The mass spectra of negative ions were obtained on the same type of instrument with an attachment for recording negative ions [18]. GLC was performed on an XT chromatograph (column 3 m × 4 mm, filled with chromaton N with 10% XE-60, carrier-gas nitrogen, 40 ml/min).

Dimerization of trimethylvinylsilane (I)

Trimethylvinylsilane (I) (2 mol) was heated to 100°C for 10 h in the presence of cobalt oxyquinolate (7×10^{-3} mol), TPP (7×10^{-3} mol) and TEA (5×10^{-2}

mol) to give a 30% yield of dimer and 45% monomer conversion of 1,4-bis(trimethylsilyl)but-1-ene (III). B.p. 90—91°C/28 mmHg, n_D^{20} 1.4350 (Lit: [19]: b.p. 81—83°C/17 mmHg; n_D^{20} 1.4354). IR spectrum (ν, cm^{-1}): 700, 760, 840, 1250, 1620, 3070. PMR spectrum (δ, ppm): 0.10 s [9 H, $-Si(CH_3)_3$], 0.15 s [9 H, $=Si(CH_3)_3$]; 0.55—0.85 m (2 H, C^4); 2.12—2.37 m (2 H, C^3); 5.40—5.85 m (2 H, CH=CH). Mass spectrum: *m/e* 200. Found: C, 60.10; H, 12.05; Si, 27.86. $C_{10}H_{24}Si_2$ calcd.: C, 60.00; H, 12.00; Si, 28.00%.

General procedure for co-oligomerizing trimethyl-(I) and trimethoxy-(II) vinylsilanes with butadiene

A cooled solution of $Ni(acac)_2$ (4×10^{-3} mol), TPP (4×10^{-3} mol) and TEA (2×10^{-2} mol) in THF (10 ml) was stirred in a flow of nitrogen for 20 min and subsequently transferred into a cooled autoclave which had been precharged with butadiene (2 mol) and silane (1 mol). The mixture was maintained at 100°C for 9—10 h, cooled to 20°C and distilled.

1-Trimethylsilyl-trans,trans-deca-1,4,9-triene (IV) *

B.p. 65—66°C/2 mmHg; n_D^{20} 1.14610. IR spectrum (ν, cm^{-1}): 700, 850—870, 1250 [$C-Si(CH_3)_3$]; 915, 975, 1000, 1605, 1650, 3020, 3080 (HC=CH). PMR spectrum (δ, ppm): 0.12 s [9 H, $Si(CH_3)_3$]; 1.40 m (2 H, C^7); 1.75—2.25 m (4 H, C^6 and C^8); 2.45—2.80 m (2 H, C^3); 4.60—6.20 m (7 H, CH=CH). Found: C, 75.20; H, 11.30; Si, 13.40. $C_{13}H_{24}Si$ calcd.: C, 75.00; H, 11.54; Si, 13.46%. Mass spectrum: *m/e* 208.

1-Trimethylsilyl-cis, trans-deca-1,4,9-triene (V) *

B.p. 72—73°C/92 mmHg; n_D^{20} 1.4613. IR spectrum (ν, cm^{-1}): 700, 850—870, 1250 [$C-Si(CH_3)_3$]; 780, 915, 975, 1000, 1605, 1650, 3020, 3080 (HC=CH). PMR spectrum (δ, ppm): 0.13 s [9 H, $C-Si(CH_3)_3$]; 1.37 m (2 H, C^7); 1.70—2.25 m (4 H, C^6 and C^8); 2.50—2.80 m (2 H, C^3); 4.50—6.20 m (7 H, CH=CH). Mass spectrum: *m/e* 208.

Desilylation of silane V

The product V (6 g) was dissolved in dry benzene (20 ml) and added to solution of $MoCl_5$ (1.74 g) in dry benzene (60 ml). The reaction mixture was heated to 40—50°C for 2—3 h. The $MoCl_5$ residue was then filtered off, the benzene evaporated and the residue distilled under vacuum. Yield: 1.6 g of known [7,8] *trans*-deca-1,4,9-triene (VI).

Hydroalumination of silanes IV and V

A 10 g mixture of IV and V (1/1) was added to DIBAH (2.5 g) at 80°C under nitrogen. The temperature was then elevated to 130°C and the reaction mixture was kept at this temperature for 18 h. The unreacted silanes (4 g) were distilled under vacuum; the resultant organoaluminium compound was hydrolyzed with water and the organic layer dried over $MgSO_4$ and distilled. Yield: 3.6 g of a mixture consisting of VII and VIII (1/1) which were isolated with the aid of preparative GLC.

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* Isolated by means of preparative GLC.

1-Trimethylsilyl-trans-deca-4,9-diene (VII)

B.p. 75—76°C/2 mmHg; n_D^{20} 1.4515. IR spectrum (ν, cm^{-1}): 700, 850, 1250 [C—Si(CH$_3$)$_3$], 915, 975, 1000, 1650, 3020, 3080 (CH=CH). PMR spectrum (δ, ppm): —0.05 s [9 H, C—Si(CH$_3$)$_3$]; 0.41 m (2 H, C^1); 1.15—1.67 m (4 H, C^2 and C^7), 1.95 m (6 H, C^3, C^6 and C^8); 4.56—5.08 m (3 H, C^9 and C^{10}); 5.26 m (2 H, C^4 and C^5). Found: C, 74.19; H, 12.36; Si, 13.28. $C_{13}H_{26}Si$ calcd.: C, 74.3; H, 12.4; Si, 13.3%. Mass spectrum: *m/e* 210.

1-Trimethylsilyl-trans-dec-4-ene (VIII)

B.p. 80—81°C/2 mmHg; n_D^{20} 1.4470. IR spectrum (ν, cm^{-1}): 700, 850, 1250 [C—Si(CH$_3$)$_3$], 975, 1650, 3020, 3080 (CH=CH). PMR spectrum (δ, ppm): —0.06 s [9 H, C—Si(CH$_3$)$_3$], 0.42 m (2 H, C^1); 1.01—1.46 m (11 H); 1.85 m (4 H, C^3 and C^6); 5.25 m (2 H, C^4 and C^5). Found: C, 73.45; H, 13.00; Si, 13.12. $C_{13}H_{28}Si$ calcd.: C, 73.6; H, 13.2; Si, 13.2%. Mass spectrum: *m/e* 212.

1-Trimethoxysilyl-cis,trans-deca-1,4,9-triene (IX)

B.p. 122°C/2—3 mmHg; n_D^{20} 1.4543. IR spectrum (ν, cm^{-1}): 680, 770, 915, 1000, 1605, 1650, 3010, 3080 (CH=CH), 1090—1100 [—Si(OCH$_3$)$_3$]. PMR spectrum (δ, ppm): 1.57 m (2 H, C^7); 1.76—2.12 m (4 H, C^6 and C^8); 3.38 s [9 H, Si(OCH$_3$)$_3$]; 2.60—3.00 m (2 H, C^3); 4.72—6.37 m (7 H, CH=CH). ^{13}C NMR spectrum (δ, ppm): 28.81 t (C^7); 32.05 t (C^6); 33.28 t (C^8); 39.43 t (C^3); 49.86 q (OCH$_3$); 114.4 t (C^{10}); 118.8 d (C^1); 126.8 d (C^5); 131.5 d (C^4); 138.0 d (C^9); 150.9 d (C^2). NIDEC mass spectrum, see Table 1. *m/e* 256. Found: C, 61.10; H, 9.40; Si, 10.90. $C_{13}H_{24}O_3Si$ calcd.: C, 60.94; H, 9.45; Si, 10.90%.

Deuterized triene X

The reaction of butadiene-d_6 with trimethylvinylsilane was carried out by the above procedure at 105°C during 14 h. Yield of deuterized derivatives of decatriene was 45%. The principal product X (ca. 52%) was isolated by GLC and had b.p. 104°C/13 mmHg; n_D^{20} 1.4602, IR spectrum (ν, cm^{-1}): 700, 730, 850—880, 910, 1000, 1250, 1605. PMR spectrum (δ, ppm): —0.02 s, —0.03 s [9 H, C—Si(CH$_3$)$_3$]; 1.93 s; 2.68 d (1 H, C^8, C^3); 5.62 s, 5.81 t (2 H, C^1, C^2). Mass spectrum: *m/e* 220.

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