INTERACTION OF BUTADIENE WITH TRIMETHYLVINYLSILANE OVER A NICKEL CHLORIDE CATALYTIC SYSTEM

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Summary

The interaction of butadiene with trimethylvinylsilane over a nickel chloride catalytic system in the presence of an organoaluminum Lewis acid and triphenylphosphine proceeds by telomerization and results in the formation of telomer homologs of general formula $(CH_3CH=CHCH_2)_nCSi(CH_3)_3=CH_2$, $n = 1$—5. The reaction is accompanied by the formation of a dimer of trimethylvinylsilane 2,4-bis(trimethylsilyl)-1-butene (ca. 5—15%).

Introduction

The interaction of 1,3-dienes with trimethylvinylsilane (TMVS) over a catalytic system comprising nickel acetylacetonate, triethylaluminium and triphenylphosphine is known to yield decatrienyl derivatives of silicon [1,2]. There is no evidence, however, for the formation of other co-oligomers in these reactions. Also, butadiene and ethylene are known to convert to hexadienes over a nickel-containing catalytic system in the presence of an organoaluminium Lewis acid [8].

Comparison of physico-chemical characteristics of the double bonds in TMVS and ethylene indicates that these bonds are of similar nature. Thus, the first ionization potentials for TMVS and ethylene are 9.8 and 10.5 eV, respectively [3,4]. As observed in ^{13}C NMP spectrum of TMVS, the difference in chemical shifts of the C_α and C_β carbon atoms in the ethylene radical is rather small ($\Delta\delta = 8$ ppm) [4]. This value may be an indication of the polarity of the double bond or, to be more precise, the increase or decrease in electron density at one of the carbon atoms of the double bond. In propylene $\Delta\delta = 18.5$ ppm [5], which testifies to a greater polarity of the double bond in propylene as compared with TMVS. Also, TMVS and ethylene display similar abilities for

π-complexing with transition metals; steric factors in TMVS have no significant effect on complexing [6,7].

Results and discussion

Considering the above-mentioned data, we chose a catalytic system consisting of nickel chloride (NiCl$_2$), triphenylphosphine (TPP), and ethylaluminium-sesquichloride (AlEt$_{1.5}$Cl$_{1.5}$) to study the reaction of butadiene and TMVS co-oligomerization. Butadiene and TMVS, on heating at 60°C for 5 hours over a catalytic system comprising NiCl$_2$, TPP and AlEt$_{1.5}$Cl$_{1.5}$ (total molar ratio $1/1/1 \times 10^{-2}/1 \times 10^{-2}/4 \times 10^{-4}$), yield a mixture of hexadienyl (C$_6$) and decatrienyl (C$_{10}$) silanes (4/1, yield 97%, TMVS conversion 42%). Mixture C$_6$ consists of two isomers (I and II, 1/3), which are isolated by preparative GLC. IR, PMR, and UV spectroscopic data indicate that both I and II have two non-conjugated disubstituted double bonds, a trimethylsilyl fragment, and a terminal methyl group at the double bond. ^{13}C NMR spectra of I and II (Fig. 1), however, proved to be especially informative. The existence of a disubstituted vinyl bond in both compounds is evidenced by the presence of triplet signals at 124 ppm and singlet signals at 150 ppm. These spectra also allow one to estimate the configuration of the second disubstituted double bond in silanes. The carbon atom of the methyl group in compound I resonates as a quartet at 17.9 ppm, while in compound II it is shifted upfield to 12.8 ppm because of the Z-configuration of the double bond [9]. The information yielded is consistent with PMR spectral data. Thus, products I and II may be formulated as 2-trimethylsilyl-E-1,4- and 2-trimethylsilyl-Z-1,4-hexadiene, respectively.

As the formation of compounds with a disubstituted vinyl bond was rather unexpected, we studied some chemical conversions of I and II. Hydrogenation of
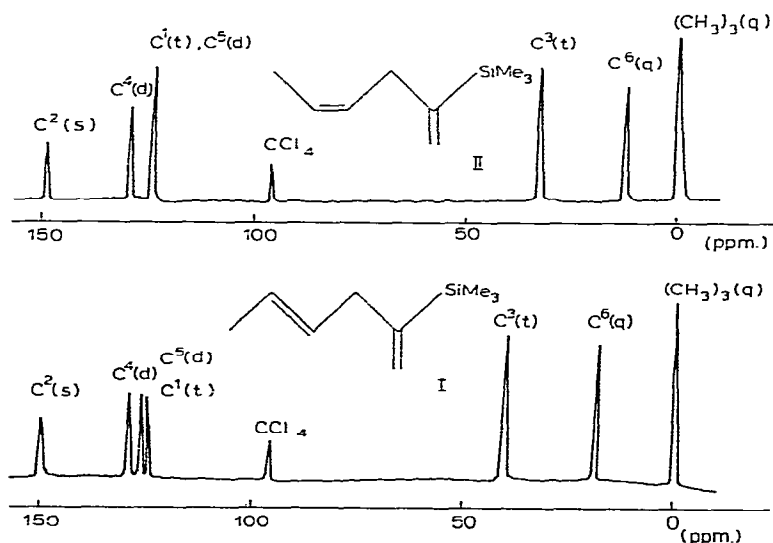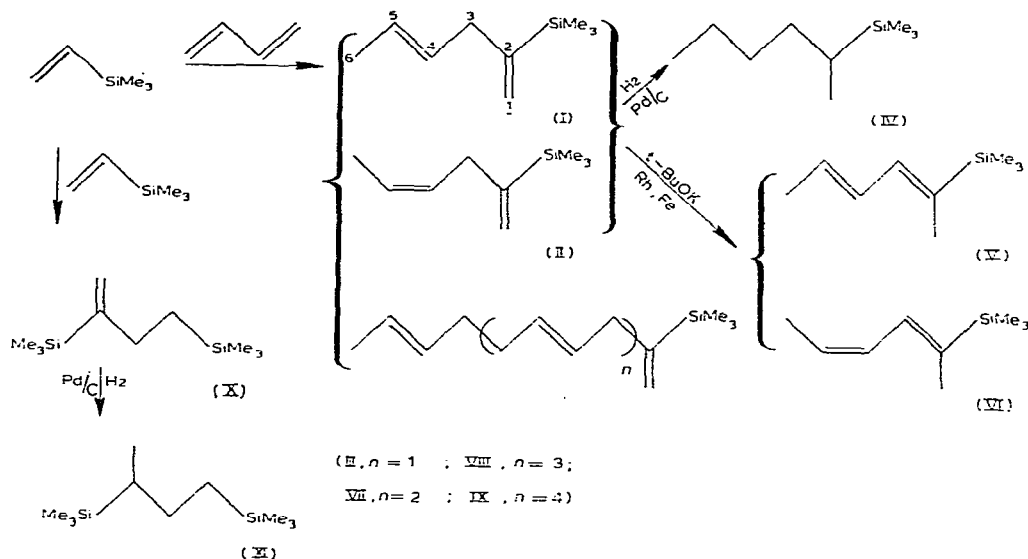

Fig. 1. ^{13}C NMR spectra 2-trimethylsilyl-E,E- (I) and 2-trimethylsilyl-E,Z- (II) 2,4 hexadienes.

a mixture of I and II over 5% Pd/C yields the known 2-trimethylsilylhexane (IV) [10].

The isomerization of the mixture of I and II was also investigated over potassium tert.-butoxide in dimethylsulphoxide (DMSO), over tris(triphenylphosphine)rhodium chloride (Rh(TPP)₃Cl) in hexamethylphosphoric triamide (HMPTA), and over iron pentacarbonyl (Fe(CO)₅) in HMPTA. These catalysts have proved to be good isomerizing agents for unsaturated compounds [11].

At a molar ratio of tert.-BuOK to silane of 1/10, the reaction yielded a mixture of conjugated isomeric silanes (V and VI, 1/3, yield 58%), and a mixture of desilylated E,E-2,4-, E-1,3- and Z-1,4-hexadienes (yield 30%). Changing the molar ratio to 1/1 led to complete desilylation of I and II, the yield of hexadienes being ca. 90%. Isomerization over Rh(TPP)₃Cl in HMPTA, at a 1/100 molar ratio of isomerizing agent to silane, led to the same silanes V and VI (1/1), while substitution of this agent by Fe(CO)₅ in the same solvent changed the ratio of V to VI to 2/1. Products V and VI were separated by preparative GLC and, on the basis of the data from physico-chemical methods of analysis (Table 2), these compounds were formulated as 2-trimethylsilyl-E,E- and 2-trimethylsilyl-E,Z-2,4-hexadiene, respectively.

From the mixture of decatrienyl silanes (C₁₀) a predominant product (III) was isolated which, in contrast to 1-trimethylsilyl-E,E-1,4,9-decatriene (XII) obtained by us earlier [2], is 2-trimethylsilyl-E,E-1,4,8-decatriene. The substances exhibited significant differences in ¹³C NMR spectra. The spectrum of III showed triplet and singlet signals of atoms C^1 and C^2 at 124.3 and 149.9 ppm, respectively; these signals are characteristic for the disubstituted vinyl bond (methylene) at C^1 (as in the case of silanes I and II). In the spectrum of XII these signals are lacking, but two doublets appear in the region 128 (C^1) and 145 (C^2) ppm, testifying to the absence of branching in the polyene. Besides, a quartet at 18 ppm in the spectrum of III can be assigned to the signal of carbon atom C^{10} of the terminal methyl group at the E-disubstituted double bond. A similar signal is not seen for XII and this is consistent with the IR data.

Increasing the temperature and time (100°C, 8 h) of the reaction of butadiene with TMVS (with the same molar proportions of the reagents) over the above mentioned catalytic system leads to the formation of the expected (C_6 and C_{10}), along with tetradecatetraenyl (C_{14}, VII) and octadecapentaenyl (C_{18}, VIII) silanes; the ratio of the silanes obtained being: $C_6/C_{10}/C_{14}/C_{18} = 3/1.5/1/1$; total yield 73%; TMVS conversion 85%. By means of a multiple distillation of a high-temperature silicon octadecapentaenyl fraction we managed to isolate a silicon oligomer mixture (C_{22}, IX) with rather low yield (ca. 9%).

Product VII (C_{14}) consists of two isomers which can be isolated preparatively. Determination of the double bond configuration in individual silanes, presents difficulties, however, since IR, PMR, UV, and mass spectra of these products are virtually identical. Therefore we limited ourselves only to the establishment of the location of the double bonds in polyene radicals of the oligomer VII. Mass spectra for the negative ions from dissociative electron capture (NIDEC) yielded, in this respect, the most clear-cut information. The NIDEC spectral data of oligomer VII are listed in Table 1.
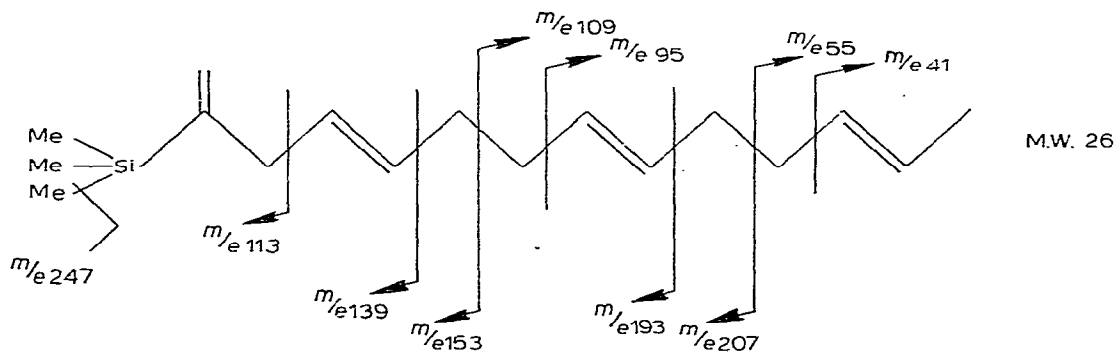
Based on the previously determined data for ion disintegration for alkenyl silanes [12], we concluded that the double bonds in the polyene chain of oligomer VII should be assigned to atoms C^1, C^4, C^8 and C^{12}. The proposed location of the double bonds is consistent with the IR, PMR, UV and ^{13}C NMP spectral

TABLE 1

MASS SPECTRUM FOR NEGATIVE IONS OF DISSOCIATIVE ELECTRON CAPTURE BY OLIGOMER (VII)

m/e	Relative intensity (%)	eV
261 ($M - H$)⁻	100	7.8
247	4.5	6.7
207	36.0	7.9
193	17.5	7.8
153	34.5	8.1
139	4.0	7.7
113	31.0	7.7
109	17.5	8.0
95	5.0	7.9
73	39.0	6.9
55	87.0	8.0
41	37.0	8.0

data for VII. The ^{13}C NMR spectrum of VII exhibits a triplet at 124 ppm and a singlet at 150 ppm which proves the existence of a disubstituted vinyl bond at C^1 carbon atom.

Oligomer VIII (C_{18}) consists of a mixture of geometric isomers of octadeca-1,4,8,12,16-pentaenyltrimethylsilane.

It should be noted that in all the experiments a dimer of TMVS (X) is formed (ca. 5—15%), its yield increasing up to 30—40% with an increase in the molar ratio of the initial reagents. The structure 2,4-bis(trimethylsilyl)-1-butene was assigned to dimer X, which became possible only after ^{13}C NMR spectra of X and its hydrogenated sample XI had been considered.

Thus, the structure of the butadiene and TMVS co-oligomers of composition 1/1 (I, II), 2/1 (III), 3/1 (VII), 4/1 (VIII), 5/1 (IX) obtained and also the absence of homooligomers of butadiene in the reaction mixture suggests that the co-oligomerization over the catalytic system investigated follows the pattern of telomerization. And though it is universally accepted that telomerization implies addition of a saturated telogen to an unsaturated taxogen, the sequence of formation of the reaction products enables us to classify the reaction type as telomerization. Thus, this reaction over a catalytic system comprising nickel chloride, triphenylphosphine and ethyl aluminumsesquichloride may be used for the laboratory synthesis of telomer homologs of butadiene and TMVS.

Experimental

IR and UV spectra were recorded on UR-20 (films) and Specord UV-vis (alcohol solutions) spectrophotometers. PMR spectra were run on a Tesla BS-487B instrument as solutions in CCl_4 (operating frequency 80 MHz) with and without proton stabilization with respect to HMDS. ^{13}C NMR spectra was obtained on a Bruker WH-90 spectrometer at 22.63 MHz with wide-band suppression along the protons and in a monoresonance mode. Chemical shifts δ (ppm) were referred to TMS; CCl_4 (69 ppm) served an internal standard. Mass spectra were determined on a MX-13-03 spectrometer (electron ionization energy 50 eV, ionization temperature 200°C). Mass spectra of negative ions were run on the same type of instrument fitted with an attachment for recording negative ions. GLC was performed on a Chrom 4 chromatograph (thermal conductivity cell), column 1.2—2.5 m × 3 mm filled with celite 503; liquid phase 10% XC-2-1, carrier-gas helium (40 ml/min). Preparative separation of silanes was conducted on a Tsvet-3-66 instrument, column 1—2 m × 14 mm filled with tsvetokhrom, liquid phase 10% XC-2-1, carrier-gas helium (120—200 ml/s).

General procedure for co-oligomerization of TMVS and Butadiene

A cooled solution of $NiCl_2$ (0.01 mol), TPP (0.01 mol), $AlEt_{1.5}Cl_{1.5}$ (0.04 mol), TMVS (0.2 mol) and butadiene (0.2 mol) was stirred for 10 min in a flow of argon and subsequently transferred into a cooled autoclave, precharged with the starting silane (0.8 mol) and butadiene (0.8 mol). The mixture was kept at 60—100°C for 5—8 h, then cooled to 20°C, and distilled.

TABLE 2

PROPERTIES OF THE COMPOUNDS OBTAINED

Com- pound	B.p. (°C) (mmHg)	n_D^{20}	IR spectra (ν, cm^{-1})	PMR spectra (δ, ppm)	13 C NMR spectra (δ, ppm)	Mass spectra (m/e)
I	161(760)	1.4434	700, 760, 840—860, 930, 980, 1255, 1610, 3020, 3060	0.00s(9 H, SiMe$_3$); 1.61d(3 H); 2.66—2.81m(2 H); 5.26—5.49m(4 H)	−1.27q(SiMe$_3$); 124.4t(C^1); 150.0s(C^2); 39.40t(C^3); 129.6d(C^4); 125.5d(C^5); 17.90q(C^6)	154
II	63—64(30)	1.4458	700, 760, 840—860, 930, 980, 1255, 1610, 3030, 3060	−0.01s(9 H, SiMe$_3$); 1.51d(3 H); 2.76m(2 H); 5.12—5.48m(4 H)	−1.37q(SiMe$_3$); 124.2t(C^1); 149.6s(C^2); 33.38t(C^3); 128.6d(C^4); 124.2d(C^5); 12.81q(C^6)	154
III	106—107(10—11)	1.4640	700, 760, 840—860, 930, 980, 1255, 1600, 1660, 3020, 3060	0.01s(9 H, SiMe$_3$); 1.52m(3 H); 1.90—2.11m(4 H); 2.62—2.87m(2 H); 5.14—5.55m(6 H)	124.3t(C^1); 149.9(C^2); 39.63t(C^3); 130.7d(C^4); 129.8d(C^5); 33.87t(C^6); 32.90t(C^7); 130.9t(C^8); 124.6d(C^9); 18.07q(C^{10}); −1.21q(SiMe$_3$)	208
V ^{a}	158(760)	1.4744	690, 760, 840—860, 950—970, 1255, 1590, 1640	0.02s(9 H, SiMe$_3$); 1.67d(3 H); 1.72d(3 H); 5.40—5.80m(1 H); 6.10—645m(2 H)	−1.75q(SiMe$_3$); 15.02q(C^1); 137.2s(C^2); 129.3d(C^3); 137.2d(C^4); 127.8d(C^5); 18.52q(C^6)	154
VI ^{b}	150(760)	1.4755	720, 760, 840—860, 950—970, 1255, 1580, 1640, 3040	0.02s(9 H, SiMe$_3$); 1.64d(3 H); 1.74d(3 H); 5.21—5.78m(1 H); 5.98—6.46m(2 H)	−2.04q(SiMe$_3$); 14.59q(C^1); 137.3s(C^2); 125.5d(C^3); 131.3d(C^4); 125.0d(C^5); 13.03q(C^6)	154
VII ^{c}	121—122(6)	1.4805	700, 770, 850—870, 930, 980, 1255, 1440, 1640, 3020, 3060	0.04s(9 H, SiMe$_3$); 1.59d(3 H); 1.87m(8 H); 2.68—2.87m(2 H); 5.15—5.62m(8 H)	−1.75q(SiMe$_3$); 123.8t(C^1); 149.6s(C^2); 39.03t(C^3); 129.2d(C^4); 129.2d(C^5); 32.36t(C^6); 32.36t(C^7); 129.2d(C^8); 129.2d(C^9); 33.27t(C^{10}); 32.36t(C^{11}); 130.3d(C^{12}); 123.8d(C^{13}); 17.54q(C^{14})	262

VIII	186(2)	1.4892	700, 770, 850—870, 940 980, 1255, 1450, 1640 3020, 3060	0.01s(9 H, SiMe₃); 1.55d(3 H); 1.96m(12 H); 2.72— 2.85m(2 H); 5.04—5.60m(10 H)		316
IX	228—230(1)	1.4930	700, 760, 850—870, 930, 980, 1255, 1450, 1640, 3020, 3060, 3080	0.02s(9 H, SiMe₃); 1.48— 1.67m(3 H); 1.90—2.12m(16 H); 2.69—2.78m(2 H); 5.11—5.45m(12 H)		
X	70—71(25)	1.4382	700, 760, 850—870, 920, 1255, 3060	0.05s(9 H, SiMe₃); 0.13s (9 H, SiMe₃); 0.48—0.78m(2 H); 1.93—2.32m(2 H); 5.18—5.68m(2 H)	-1.09q(SiMe₃); 1.41q (SiMe₃); 122.4t(C^1); 153.5s(C^2); 29.99t(C^3); 16.33t(C^4)	200
XI	82—83(25)	1.4288	700, 760, 850—870, 1255 1420, 1480	-0.1s(9 H, SiMe₃); -0.08s (9 H, SiMe₃); 0.41—0.67m(3 H); 0.88d(3 H); 1.03— 1.20m(2 H)	-2.33q(SiMe₃); -0.97q (SiMe₃); 16.37t(C^1); 26.60t(C^2); 23.75d(C^3); 14.38q(C^4)	202
XII	65—66(2)	1.4610	700, 850—870, 1250, 915 975, 1000, 1605, 1650	0.12s(9 H, SiMe₃); 1.40m(2 H); 1.75—2.25m(4 H); 2.45—2.70m(2 H); 4.60— 6.20m(7 H)	-0.52q(SiMe₃); 127.9d(C^1); 145.1d(C^2); 40.06t(C^3); 131.2d(C^4); 130.3d(C^5); 32.49t(C^6); 29.49t(C^7); 33.72t(C^8); 138.1d(C^9); 114.7t(C^{10})	208

[a] UV spectrum of V (λ_{max}(EtOH)): 241 nm (lg ε 4.17), [b] UV spectrum of VI (λ_{max}(EtOH)): 246 nm (lg ε 4.27), [c] UV spectra of VII (λ_{max}(EtOH)): 238 nm (lg ε 2.95), ¹³C NMR spectrum of VII shows signals of the carbon atoms of the predominant product, 2-trimethylsilyl-E,E,E-1,4,8,12-tetradecatetraene.

Isomerization of a mixture of trimethylsilylhexadiene I and II

1. Potassium tert-butoxide in DMSO

(a) A 0.05 mol mixture of silanes I and II (I/II = 1/3) in 8 ml DMSO was added at 55°C (stirring in a inert atmosphere) to a 0.05 mol solution of potassium tert-butoxide in DMSO. The mixture was kept at this temperature for 3 hours, cooled, hydrolysed with water, and extracted with pentane, and diethyl ether., The organic layer was dried over $MgSO_4$, solvents evaporated, and the residue distilled under vacuum to give a mixture of the following composition: 30% desilylated isomeric hexadienes (*E,E*-2,4-; *E*-1,3-; *Z*-1,4-); 12% unreacted initial silanes I and II; and 58% isomeric conjugated trimethylsilylhexadienes V and VI (V/VI = 1/3). Products V and VI were isolated by preparative GLC.

(b) Conducting the experiment according to procedure (a), but with a 1/2 molar ratio of potassium tert--butoxide to the mixture of silanes I and II, at 60°C for 1.5 h leads to the formation of desilylated hexadienes (ca. 90%).

2. Complexes of transition metals in HMPTA

(a) Rh(TPP)₃Cl in HMPTA. 0.1 mol of a mixture of silanes (I/II = 1/3) was added at 130—140°C (stirring in an inert atmosphere) to the solution of 0.001 mol $Rh(TPP)_3Cl$ in 10 ml HMPTA. The reaction mixture was kept at this temperature for 9 hours, then cooled, filtered off from the catalyst and distilled under vacuum; yield of isomerization products V and VI was 62% (V/VI = 1/1). Further increase in the reaction time to 21 hours failed to improve the yield of the isomeric silanes V and VI.

(b) Fe(CO)₅ in HMPTA. Conducting the isomerization at a 0.7/1.0 molar ratio of $Fe(CO)_5$ to the mixture of silanes I and II in HMPTA solution at 110—120°C for 10-12 hours results in the formation of V and VI (V/VI = 2/1), yield 31%.

Constants and physico-chemical data of the compounds obtained are listed in Table 2.

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