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OLIGOMERIZATION OF VINYL- AND ETHYNYL-TRIMETHYLSILANES

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Summary

Oligomerization of vinyl- and ethyl-trimethylsilanes in the presence of homogeneous nickel, cobalt and titanium catalytic systems has been studied. Vinyltrimethylsilane forms linear dimeric products, 1,4-bis(trimethylsilyl)butenes. Using the titanium catalytic system, in addition to butenyldisilane, a branched dimeric product, 1,3-bis(trimethylsilyl)-3-methylprop-1-ene, and a linear trimer 1,3,6-tris(trimethylsilyl)hex-3-ene are formed. Ethynyltrimethylsilane, in the presence of the nickel catalytic system, is converted into a linear dimer, 1,4-bis-(trimethylsilyl)but-3-ene-1-yne, and linear trimer, 1,4,6-tris(trimethylsilyl)hex-3,5-diene-1-yne.

Introduction

Unlike dimerization of α-olefins, oligomerization of the readily available vinyl- and ethynyl-trimethylsilanes (VTMS and ETMS) has almost been completely neglected [1,2]. Their potential application for preparing compounds containing two ore more silicon groups is, however, of great interest. According to the literature [3], VTMS dimerizes on heating with triisobutylaluminum to give 1,4-bis-(trimethylsilyl)but-1-ene.

Results and discussion

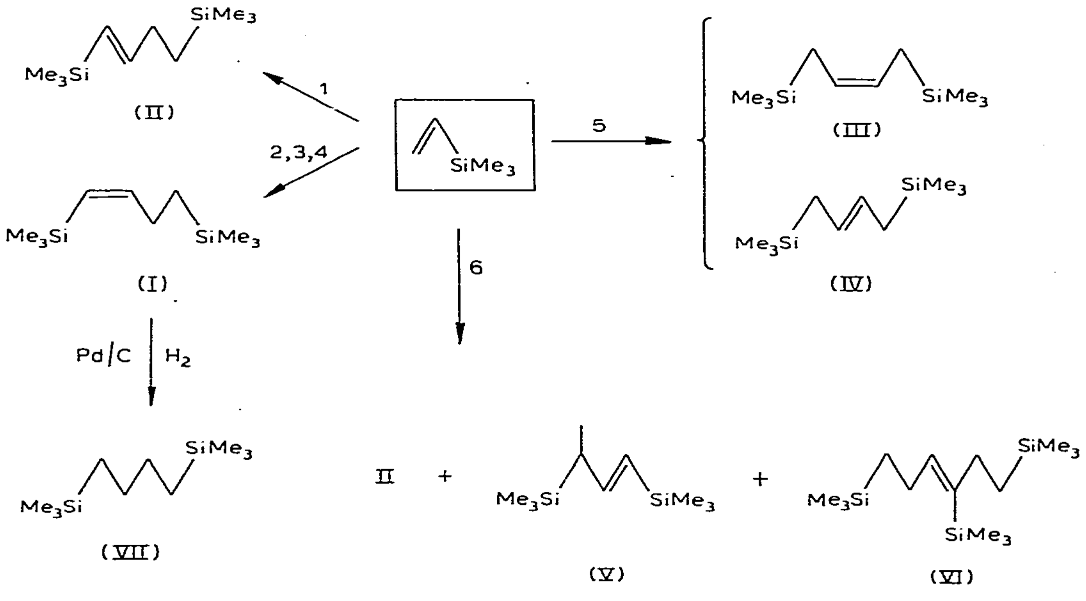
Oligomerization of VTMS and ETMS in the presence of metal complex catalysts based on nickel, cobalt and titanium were studied. These catalytic systems were selected on the basis of their high activity in dimerization and oligomerization of α-olefins [4—8].

Using the catalytic system prepared by treating cobalt 8-hydroxyquinolate with triethylaluminum (TEA) in the presence of triphenylphosphine (TPP), VTMS gives *cis*-1,4-bis(trimethylsilyl)but-1-ene (I) in a small yield (30%) at

VTMS conversion of 45%. Substitution of TPP with triphenylstibine (TPS) in this complex results in formation of the *trans*-isomer (II) in the same yield. When TPP is used as a ligand-activator, in addition to dimer I, 3—5% of *trans*-trimethylsilylbut-2-ene is formed. Formation of the latter probably occurs by desilylation of dimer I in the presence of the catalyst. Varying the ratio between components of the catalytic complex and initial reagent, changing the reaction conditions or the use of polar solvents (tetrahydrofuran and ether) do not increase the yield of I.

The catalytic system prepared by TEA reduction of nickel acetylacetonate, $Ni(acac)_2$, in the presence of TPP using dichloroethylene as a solvent, displays high activity. In the presence of this catalyst VTMS forms a mixture of products III : IV 1/1 in 86% yield. According to PMR data III and IV are isomeric 1,4-bis(trimethylsilyl)but-2-enes. The PMR spectrum exhibits two equal signals of the 18 methyl protons at the silicon atom (δ —0.02 and +0.04 ppm), a multiplets signal from the four protons at C(1) and C(4) in the region of δ 1.49—1.70 ppm and a multiplet from the two olefinic protons at C(2) and C(3) (δ 5.45—6.08 ppm). The absence of signals in the regions δ 0.3—0.5 and 1.8—2.00 ppm makes it possible to exclude isomers with a double bond adjacent to the silyl radical. On the basis of IR data, isomers III and IV were assigned *cis*- and *trans*-configurations, respectively. Mass spectrometric analysis of this mixture gives

SCHEME 1



1 $Co(OX)_2$, TEA , TPS
2 $Co(OX)_2$, TEA , TPP
3 $NiCl_2$, $AlEtCl_2 \cdot AlEt_2Cl$, TPP

4 $Ni(acac)_2$, $HSiCl_3$, TPP
5 $Ni(acac)_2$, TEA , TPP , $C_2H_2Cl_2$
6 $Ti(OC_4H_9)_4$, TEA , TPP

m/e 200. The use of a solvent is a necessary condition since the reaction using the nickel system does not proceed in its absence.

The catalytic activation by a chlorine-containing solvent reacts with Et_3Al to give ethylaluminum chlorides via a substitution reaction (eq. 1). Such reactions are known to be catalyzed by Ni compounds.

$$CHCl{=}CHCl + Et_3Al \xrightarrow{Ni} CHCl{=}CHEt + Et_2AlCl \qquad (1)$$

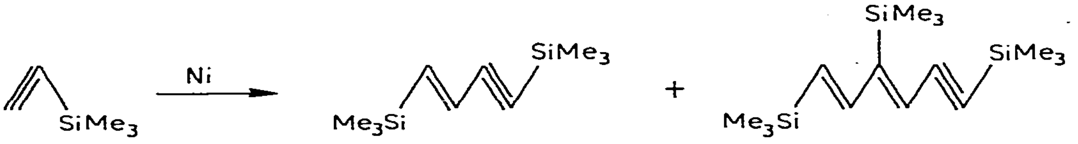
Introduction of a Lewis acid enhances activity, as was observed for certain catalysts of ethylene and propylene dimerization [4—6] and of codimerization of 1,3-dienes with ethylene [9—10]. To confirm participation of ethylaluminum chlorides in the oligomerization reaction, we examined VTMS conversion on a catalytic system prepared by reduction of nickel chloride with aluminum sesquichloride in the presence of TPP. Dimer I was obtained in 80% yield at 71% conversion of VTMS.

As titanium catalytic systems are highly selective towards ethylene dimerization [8] we used a complex prepared by reduction of tetrabutoxytitanium with TEA in the presence of TPP and and absence of a solvent. A mixture of II, V and VI (2/3/1) was obtained in 50% yield at 50% VTMS conversion. All compounds were isolated by preparative GLC. According to IR, PMR and mass spectrometric data, the structures of *trans*-1,4-bis(trimethylsilyl)but-1-ene, 1,3-bis(trimethylsilyl)-3-methyl-*trans*-prop-1-ene and 1,3,6-tris(trimethylsilyl)hex-3-ene were assigned to II, V and VI, respectively. The titanium system is the only one on which formation of trimer VI was established.

Oligomerization of VTMS in the presence of a catalytic system which excludes the use of organoaluminum reducing agents was also studied. Such systems are highly active in hydrosilylation of dienes [11]. Thus, in the presence of a catalytic system including $Ni(acac)_2$, trichlorosilane as a reducing agent and TPP, VTMS is converted into dimer I in 30% yield.

Hydrogenation of 1,4-bis(trimethylsilyl)-*cis*-but-1-ene (I) in the presence of 5% Pd/C in diethyl ether gave the known [12] 1,4-bis(trimethylsilyl)butane (VII). Desilylation of dimer I by $MoCl_5$ in benzene [13] resulted in formation of but-1-ene and trimethylchlorosilane. Attempts to carry out fractional desilylation failed, even at room temperature two trimethylsilyl fragments are simultaneously eliminated within an hour. Attempts to oligomerize vinyltrichloro-, vinyltrimethoxy- and allyltrimethyl-silanes were unsuccessful.

ETMS undergoes oligomerization reactions much more readily than VTMS, to form, at lower temperatures and higher rates the linear dimer 1,4-bis(trimethylsilyl)but-3-ene-1-yne (VIII) and the linear trimer 1,4,6-tris(trimethylsilyl)hexa-3,5-diene-1-yne (IX) in the presence of a catalytic system consisting of $Ni(acac)_2$,



(2)

(VIII) (IX)

TPP and TEA (eq. 2). At 40°C after 2 hours ETMS is converted into VIII and

IX (1 : 1), yield 65% at 67% ETMS conversion. At 70°C the same products are formed but in a VIII : IX 1 : 3 ratio; the yield is 60% at 90% conversion. At room temperature the composition of the reaction products does not change but the yields and conversions are very low (≈10—15%). Higher temperatures (120°C) increase the yield of higher oligomeric products, the yield of VIII and IX being ≈30%. The cobalt-containing system was found to be not very active towards oligomerization reactions.

Experimental

IR and UV spectra were recorded on UR-20 (films) and Specord UV-vis (alcohol solutions) spectrophotometers. PMR spectra were obtained with a Tesla BS-487B instrument, working frequency 80 MHz, CCl_4 solutions with and without HMDS. Mass spectra were recorded on a MX-13-03 instrument, ionization energy 50 eV, ionization temperature 200°C. GLC analyses were performed on a XT-63 instrument, phase XE-60, 10% on Chromosorb W.

Oligomerization of VTMS

(1) In the presence of the Co-containing catalytic system.

(a). The complex prepared from cobalt hydroxyquinolate (3.5×10^{-3} mol), TPP (2.5×10^{-3} mol) and TEA (2.5×10^{-2} mol) was stirred for 20 min in a flow of dry nitrogen whilst slightly cooling, and then transferred to an autoclave loaded with VTMS (1 mol). The mixture was heated to 100°C and kept for 10 h. The autoclave was then cooled to 20°C and the mixture distilled under vacuum. *cis*-1,4-Bis(trimethylsilyl)but-1-ene (I) was obtained, 30% yield, 45% conversion of VTMS, b.p. 90—91°C/28 mmHg, n_D^{20} 1.4350. IR spectrum (ν, cm^{-1}): 700, 840, 1250 ($Si(CH_3)_3$); 760, 1610, 3070 (CH=CH). PMR spectrum (δ, ppm): 0.10 s (9H, $Si(CH_3)_3$), 0.15 s (9H, $Si(CH_3)_3$); 0.55—0.85 m (2H, C(4)); 2.12—2.37 m (2H, C(3)); 5.40—5.85m (2H, C(1), C(2). M^+ 200 (mass spectrometry). (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%.) Lit.: b.p. 81—83°C/17 mmHg; n_D^{25} 1.4354 [3].

(b). On replacement of TPP with TPS under conditions of experiment (*a*) *trans*-1,4-bis(trimethylsilyl)but-1-ene (II) was obtained, b.p. 52—53°C/3 mmHg, n_D^{20} 1.4375. IR spectrum (ν, cm^{-1}) 710, 850—870, 1260 ($Si(CH_3)_3$), 950, 1610, 3020 (CH=CH). PMR spectrum (δ, ppm): —0.02 s (9H, $Si(CH_3)_3$); —0.06 s (9H, $Si(CH_3)_3$); 0.42—0.68 m (2H, C(4)), 1.80—2.20 m (2H, C(3)); 5.50—5.70 m (2H, C(1), C(2). M^+ 200 (mass spectrometery). (Found: C, 60.10; H, 11.81; Si, 28.12. $C_{10}H_{24}Si_2$ calcd.: C, 60.00; H, 12.00; Si, 28.00%.)

(2) In the presence of the Ni-containing catalytic system

(a). The complex prepared from $Ni(acac)_2$ (1×10^{-2} mol), TPP (1×10^{-2} mol) and TEA (4×10^{-2} mol) in 25 ml of dichloroethylene was cooled in a flow of dry nitrogen and transferred to an autoclave containing VTMS (1 mol). The reaction mixture was heated to 120°C and kept at that temperature for 9 h. Vacuum distillation gave a mixture of IV and V (1/1 ratio, yield 86%, VTMS conversion

76%, b.p. 90—91°C/28 mmHg, n_D^{20} 1.4412). IR spectrum (ν, cm^{-1}): 700, 850—870, 1260 ($Si(CH_3)_3$), 770, 1050, 1150, 1610, 3020 (CH=CH). PMR spectrum (δ, ppm): —0.02 s (9H, $Si(CH_3)_3$), 0.04 s (9H, $Si(CH_3)_3$), 1.49—1.70 m (4H, C(1), C(4)), 5.45—6.08 m (2H, C(2), C(3)). M^+ 200 (mass spectrometry). (Found: C, 60.18; H, 11.96; Si, 28.20. $C_{10}H_{24}Si_2$ calcd.: C, 60.00; H, 12.00; Si, 28.00%.)

(b). In the presence of the complex obtained from $NiCl_2$ (5×10^{-3} mol), aluminium sesquichloride (3.8×10^{-2} mol) and TPP (5×10^{-3} mol) VTMS is converted into I yield 80%. VTMS conversion 71%.

(c). The complex prepared from $Ni(acac)_2$ (0.4×10^{-2} mol), $HSiCl_3$ (0.8×10^{-2} mol) and TPP (0.5×10^{-1} mol) was placed in an autoclave and heated for an hour at 120°C. The autoclave was then cooled, VMTS was introduced in a nitrogen flow (1 mol) and the reaction mixture was heated for 10 h at 100°C. Vacuum distillation rendered I yield 30%, VTMS conversion 20%.

(3) In the presence of the Ti-containing catalytic system

The complex prepared from $Ti(OC_4H_9)_4$ (5×10^{-3} mol), TPP (5×10^{-3} mol), TEA (2×10^{-2} mol) and VTMS (1 mol) was heated in an autoclave for 8 h at 100°C. Vacuum distillation gave a mixture of II, V and VI (ratio 2/3/1), total yield 50%, VTMS conversion 50%. All compounds were isolated by preparative GLC. *trans*-1,3-Bis(trimethylsilyl)-3-methylprop-1-ene (V), b.p. 70°C/25 mmHg, n_D^{20} 1.4410. IR spectrum (ν, cm^{-1}): 850—870, 1250 ($Si(CH_3)_3$), 1000, 1600, 3020 (CH=CH). PMR spectrum (δ, ppm) —0.01 s (9H, $Si(CH_3)_3$); 0.07 s (9H, $Si(CH_3)_3$; 1.09 d (3H, C(3), J = 7 Hz); 1.54—1.82 m (1H, C(3), 5.35—6.13 m (2H, olefin). 1,3,6-Tris(trimethylsilyl)hex-3-ene (VI), b.p. 115—116°C/5—6 mmHg, n_D^{20} 1.4584. IR spectrum (ν, cm^{-1}): 850—880, 1250 ($Si(CH_3)_3$); 1610, 3010 (CH=CH). PMR spectrum (δ, ppm): —0.08s (9H), —0.06s (9H), 0.01s (9H); 0.24—0.67 m (4H, C(1) and C(6)); 1.81—2.12 m (4H, C(2) and C(5)); 4.96 m (1H, C(4)). M^+ 300 (mass spectrometry). (Found: C, 60.18; H, 12.05; Si, 27.93. $C_{15}H_{36}Si_3$ calcd.: C, 60.00; H, 12.00; Si, 28.00%.)

Hydrogenation of I and II on 5% Pd/C in diethyl ether yields 1,4-bis(trimethylsilyl)butane (VII), b.p. 56°C/4 mmHg, n_D^{20} 1.4278. IR spectrum (ν, cm^{-1}): 840—860, 1255 ($Si(CH_3)_3$), 1420, 2690 (—CH_2—). PMR spectrum (δ, ppm): —0.07 s (18H, $Si(CH_3)_3$), 0.38—0.58 m (4H, C(1) and C(4)), 1.40—1.63 m (4H, C(2) and C(3)). M^+ 202 (mass spectrometry).

Oligomerization of ETMS in the presence of the Ni-containing catalytic system.

The complex prepared from $Ni(acac)_2$ (5×10^{-3} mol), TPP (5×10^{-3} mol) and TEA (2×10^{-2} mol) was placed in a cooled autoclave in a flow of nitrogen and ETMS was then added (1 mol). The autoclave was heated for 2 h at 40°C. Vacuum distillation gave a mixture of VIII and IX (ratio 1 : 1), yield 65%, ETMS conversion 67%. Compounds VIII and IX were isolated by fractional distillation under vacuum. 1,4-Bis(trimethylsilyl)but-3-ene-1-yne (VIII), b.p. 91—92°C/15 mmHg, n_D^{20} 1.4675. IR spectrum (ν, cm^{-1}): 760, 840, 1260 ($Si(CH_3)_3$), 980, 1580, 3010 (CH=CH), 2180 (C≡C). PMR spectrum (δ, ppm): 0.01 s (9H, $Si(CH_3)_3$); 0.06 s (9H, $Si(CH_3)_3$); 5.95 s (1H); 6.13 s (1H). λ_{max} (alcohol) 286 nm; lg ϵ 3.00. M^+ 196 (mass spectrometry). (Found: C, 60.15; H, 10.31; Si, 28.70. $C_{10}H_{20}Si_2$ calcd.: C, 61.20; H, 10.20; Si, 28.60%.) 1,4,6-Tris(trimethylsilyl)hex-3,5-diene-1-yne (IX), b.p. 143—144°C/6 mmHg; n_D^{20} 1.4932. IR spectrum (ν, cm^{-1}): 770, 840, 1265 ($Si(CH_3)_3$), 990, 1540, 3020 (CH=CH), 2140 (C≡C). λ_{max} (alcohol) 286, 255, 247 nm; lg ϵ 4.29, 3.93, 3.81. PMR spectrum (δ, ppm): 0.05 s (9H); 0.10 s (9H); 0.18 s (9H); 5.80 s (1H); 5.91 s (1H); 6.11 s (1H). M^+ 294 (mass spectrometry). (Found: C, 61.35; H, 10.28; Si, 28.33. $C_{15}H_{30}Si_3$ calcd.: C, 61.35; H, 10.20; Si, 28.50%.)

Hydrogenation of IX on 5% Pd/C in diethyl ether yields 1,4,6-tris(trimethylsilyl)hexane (X), b.p. 264°C/760 mmG; n_D^{20} 1.4532. IR spectrum (ν, cm^{-1}): 756, 840—860, 1260 ($Si(CH_3)_3$); 1420, 2960 (—CH_2—). PMR spectrum (δ, ppm): —0.11 s (9H); —0.09 s (9H); 0.05 s (9H); 0.20—0.55 m (5H, C(1), C(4), C(6); 1.10—1.60 m (6H, C(2), C(3) and C(5)). M^+ 302 (mass spectrometry).

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