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CATALYTIC PROPERTIES OF IRON TETRACARBONYL T-COMPLEXES OF

VINYLSILANES IN THE ADDITION OF POLYHALOMETHANES AND

HYDROSILANES TO VINYLSILANES

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Metal carbonyls catalyze the addition of alkenes to polyhalomethanes [1-5] and hydrosilanes [6, 7]. The telomerization of alkenes on $Fe(CO)_5$ with the participation of nucleophilic solvents has been studied in greatest detail. In particular, Freidlina et al. [5] studied the reaction of propylene with CCl₄ in the presence of $Fe(CO)_5$ with nucleophilic additives and proposed that the catalyst activation for both initiation and Cl radical requires prior introduction of the monomer and telogen into the iron ligand sphere.

We have previously shown that the introduction of such activators as alcohols, amides, and tertiary phosphines is also necessary for the successful reaction of vinylsilanes with polyhalomethanes on $Fe(CO)_5$ [8].

According to Schroeder and Wrighton [7], the reaction of alkenes with hydrosilanes on $Fe(CO)_5$ includes a step involving the formation of a coordinatively unsaturated $Fe(CO)_4$ fragment from $Fe(CO)_5$ upon irradiation with subsequent conversion into the catalytically active alkene ...Fe(CO)_3...HSiR_3 complex. On the other hand, hydrosilylation of vinyltrimethyl-silane in the presence of $Fe(CO)_5$ does not proceed at 40-70° [9]. Thus, both reactions are likely catalyzed by a complex containing a $Fe(CO)_n$ fragment ($n \leq 4$).

We checked this proposal by studying the catalytic activity of $Fe(CO)_4 \cdot (CH_2=CHSiR_3)$ complexes [10] in the addition of vinylsilanes to polyhalomethanes and silane hydrides.

In the present communication, we present the results of a study of the catalytic activity of $(R_3SiCH=CH_2)\cdot Fe(CO)_4$ complexes (R = Me, OMe, and the polysiloxane group) in the telomerization of vinyltrimethyl (VTMS), vinyltrimethoxy- (VTMOS), divinyldimethyl- (DVDMS), and tetravinylsilanes (TVS) with CCl₄, CHBr₃, and CHCl₃.

Table 1 shows that all the reactions, with the exception of the reaction with $CHCl_3$, catalyzed by π -complexes, proceed under milder conditions at 60-80°C for 4 h and do not require nucleophilic and donor additives relative to use of the $Fe(CO)_5$ -cocatalyst [8]. Thus, a mixture of products is formed in the reaction of VTMS with CCl₄ consisting of a 1:1 addition adduct (I), two diastereomeric dimeric telomers (VTMS:CCl₄ = 2:1) (II) and (III), and their dehydrochlorination products (IV) and (V) with (I):(II):(IV):(V) = 4:1:1:1.5:1.5, which we have reported previously [8].

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tracarbonyl m-Com-	ts Yield (silane con-	$\begin{array}{c} (V) = \\ 65 (83) \\ 15 (76) \\ 9 (86) \\ 8 (477) \\ 8 (477) \\ 8 (477) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (47) \\ 8 (48) \\ 8 (48) \\ 10 (28) \\ 8 (50) \\ 13 (40) \\ 15 (36) \\ 14 (23) \\ 8 (50) \\ 13 (40) \\ 15 (36) $
ction of Vinylsilanes with Polyhalomethanes in the Presence of Iron Te ylsilanes (80°C, 4 h, 1:1 vinylsilane/halomethane molar ratio)	Reaction produc	(1):(11):(11):(11):(11):(11):(11):(11):
	Catalyst/vinylsilane molar ratio	0,020:1 0,020:1 0,022:1 0,022:1 0,022:1 0,025:3:1 0,025:3:1 0,025:3:1 0,025:3:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1 0,025:1
	Catalyst	
	Halomethane	CGI4 CGI4 CGI4 CGI4 CHBr5 Same Same Same Same CHCI3 CHCI3
TABLE 1. Rea plexes of Vin	Vinylsilane	VTMS TVS VTMS VTMS VTMS The same * * * * * * * * * * * * * * * * * * *

ron Tetracarbonyl m-Com-	
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ila	. 4
yls	0°C
Vin	8
ч Ч	nes
цо	ila
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Rea	Vin
•	Jo
 []	es Se
BLJ	ext

*Reaction temperature 60°C. †Reaction temperature 120°C in autoclave.

$$\begin{array}{c} R^{2} \\ & \swarrow SiR_{3} + CR^{1}R_{3}^{2} \rightarrow R^{1}R_{2}^{2} \\ & (I), (VI), (VIII) - (XIII) \\ & (II), (VI), (VIII) - (XIII) \\ & (II), (III) \\ & (II), (III) \\ & (II), (VI), (VIII) - (XIII) \\ & (II), (III) \\ & (II), (III) \\ & (IV), (V) \\ R = Me, OMe, R^{1} = R^{2} = CI \\ & R^{1} = R^{2} = CI, R = Me (I); \\ R^{1} = R^{2} = CI \\ & R^{1} = R^{2} = CI, R = Me (I); \\ R^{1} = R^{2} = CI, R = OMe (VI); \\ R^{1} = H, R^{2} = Br, R = OMe (VI); \\ R^{1} = H, R^{2} = Br, R = Me (IX); \\ R^{1} = H, R^{2} = Br, R = OMe (X); \\ R^{1} = H, R^{2} = Br, R = Vin (XI); \\ R^{1} = H, R^{2} = Br, R = Vin (XI); \\ R^{1} = H, R^{2} = Br, R = Vin (XI); \\ R^{1} = H, R^{2} = CI, R = Me (XII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{1} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = Me (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII) \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2} = CI, R = ME (XIII); \\ R^{2} = H, R^{2$$

The reaction of VTMOS with CCl₄ proceeds even less selectively. At high VTMOS conversion, the 1:1 adduct (VI) and a mixture of dimeric telomers, their dehydrochlorination products and a side product, vinyldimethoxysiloxane (VII) are formed in low yield. This is attributed to the high lability and hydrolytic instability of the starting silane. Preparative separation of the dimeric telomers and their dehydrochlorination products is complicated by their instability and various transformations.

TVS is a more active monomer than VTMS and VTMOS and, thus, its reaction with CCl₄ occurs to a much greater extent (86% TVS conversion). However, we were only able to isolate the 1:1 adduct (VIII) in low yield (8-10%); the remaining products polymerize upon separation.

Vinylsilanes react with CHBr3 with high selectivity to yield only 1:1 adducts. To improve the adduct yield, we varied the reaction conditions. Table I shows that a reduction in the temperature for the reaction of VTMS with CHBr3 from 80° to 60°C leads to a sharp decrease in the VTMS conversion from 47 to 18% but the reaction selectivity is maintained. The yield of adduct (IX) is reduced by almost one-half with a decrease in the vinylsilane/catalyst molar ratio from 0.025:1 to 0.017:1. The introduction of triphenylphosphine (TPP) as a cocatalyst to the π -complex does not lead to a change in the monomer conversion and yield of adduct (IX). The addition of dimethylformamide (DMF) facilitates an increase in the reaction selectivity but the VTMS conversion drops from 47 to 27%. The addition of TPP and DMF when using $Fe(CO)_5$ is necessary since the addition of halomethanes to vinylsilanes does not proceed without them [8]. The effect of these additives levels off when using π -iron tetracarbonyl complexes of vinylsilanes as catalysts. The activating role of the additives apparently is primarily related to facilitation of the formation of coordinatively unsaturated Fe(CO)₄ species from Fe(CO)₅ which are capable of complexation with vinylsilane. The π complex, in turn, is the initial catalytic form which activates the initiation step. In addition, we showed that $Fe_2(CO)_9$, in contrast to $Fe(CO)_5$, catalyzed the addition of VTMS to CHBr₃ with the formation of (IX) in 45% yield. Even at $30-40^{\circ}C$, Fe₂(CO)₉ decomposes into $Fe(CO)_5$ and $Fe(CO)_4$. The addition of TPP to $Fe_2(CO)_9$ reduces the yield of (IX) to 22%. We may assume that the coordination of TPP to $Fe(CO)_4$ is more favorable than to vinylsilane [11].

The reaction of vinylsilanes with $CHCl_3$ does not proceed on the complexes studied at 80°C. The reaction was performed in an autoclave at 120°C on π -complexes with added TPP, i.e., in a manner similar to that on the Fe(CO)₅-TPP system [8].

Hence, iron tetracarbonyl π -complexes of vinylsilanes are catalytically active molecules which activate the formation of primary HCBr₂ radicals in the oxidation-reduction reaction

$$(R_{3}SiCH = CH_{2}) \cdot Fe(CO)_{4} + HCBr_{3} \rightarrow$$
$$(R_{3}SiCH = CH_{2}) \cdot Fe(CO)_{4} \dots CHBr_{3} \rightarrow$$
$$(R_{3}SiCH = CH_{2}) \cdot Fe(CO)_{4-n} \cdot Br_{m} + HCBr_{2} + nCO$$

The mechanism for the electron transfer in this step is not yet clear.

We also studied the $(Me_3SiCH=CH_2) \cdot Fe(CO)_4$ complex as a catalyst for the addition of $HSiCl_3$, $HSiCl_2Me$, $HSiClMe_2$, and $HSiMe_3$ to VTMS. Table 2 shows that these reactions result in the formation of a mixture of products consisting of the adducts of α - and β -addition, the dehydrocondensation product, and ethyltrimethylsilane (ETMS). The product ratio depends on the hydrosilane used. The hydrosilylating activity of the hydrosilanes relative to VTMS decreases in the series $HSiCl_3 > HSiCl_2Me > HSiClMe_2 > HSiMe_3$ and the yield of the dehydrocondensation product increases. However, the predominant formation of the hydrosilylation

TABLE 2. Reaction of Vinyltrimethylsilane with Hydrosilanes in the Presence of $(CH_2=CHSiMe_3)$ ·Fe $(CO)_4$ at 70-80°C for 3 h (VTMS:hydrosilane molar ratio = 1:1.5)

Hydr osilan e	π -Complex:	VTMS conver- sion, %	Reaction products, Mo			
	v iny lsi lane		hydrosilylation		dehydrocon-	ethyltrimethyl
•	ratio		a-isomer	β −i somer	densation	
HSiCl ₃ HSiCl ₂ Me HSiClMe ₂ HSiMe ₃	0,025 : 1 0,05 : 1 0,05 : 1 0,033 : 1	72 78 80 88	68 (XIV) 61 (XVIII) 34 (XXI) 2 (XXV)	7 (XV) 8 (XIX) 5 (XXII) 4 (XXV)	12 (XVI) 18 (XX) 32 (XXIII) 60 (XXVI)	$13 \\ 13 \\ 29 \\ 34$

 α -adduct relative to the β -isomer is found in all cases

 $\begin{array}{c} \swarrow SiMe_3 + HSiRR_2^1 \rightarrow \\ R = R^1 = Cl \\ R = R^1 = Me \\ R = Me, R^1 = Cl \\ R = R^1 = Me \\ R = Cl, R^1 = Cl \\ R = Cl, R^1 = Me \\ (XVII) \\ (XVI), (XVIII), (XV), (XIX), (XVI), (XXI), (XVI), (XXI), (XVI), (XXI), (XXV) \\ (XXI), (XXIV) \\ (XXI), (XXIV) \\ R = R^1 = Cl (XIV) - (XXII), (XXV) \\ R = Cl, R^1 = Me (XXI) - (XXIII); \\ R = R^1 = Me (XXIV) - (XXVI) \\ \end{array}$

An exception is found for the reaction of VTMS with HSiMe₃ which results in the formation of 0.60% of the dehydrocondensation product (XXVI), 34% ETMS (XVII), and 6% α - and β - adducts (XXIV) and (XXV).

These reactions are not catalyzed by $Fe(CO)_5$ under our conditions (70-80°C). In addition, the composition of the reaction products obtained in the catalysis of the π -complex is similar to that of the $Fe(CO)_5$ -photocatalyzed reaction of alkenes with trialkylsilanes [7].

Stoichiometric reaction of the starting π -complex with HSiCl₃ at room temperatures does not lead to the formation of hydrosilylation products though the complex undergoes several transformations as seen by a change in the carbonyl bands in the IR spectrum. Hydrosilylation products appear at 50-60°C.

All these findings forced us to propose that $Fe(CO)_4 \cdot (CH_2 = CHSiMe_3)$ is the initial catalytic form which upon reaction with a hydrosilane forms the key unstable hydride complex (A) which undergoes further transformations



The results for the reaction of VTMS with various hydrosilanes on $Fe(CO)_4 \cdot (CH_2 = CHSiMe_3)$ indicate the following reaction scheme by analogy with Schroeder [7]:



Thus, the catalytic cycle leading to hydrosilylation products consists of oxidative addition with the formation of hydride forms of complex (A), insertion with the formation of σ -complexes (B) and (C), reductive elimination, and generation of the original species (A). On the other hand, intermediate (C) may reversibly generate the dihydride complex (D) responsible for the formation of dehydrocondensation products and a new dihydride complex (E), which reversibly converts to the σ -alkyl intermediate (F) which gives the hydrogenation product of VTMS in reductive elimination with generation of the starting complex (A).

EXPERIMENTAL

The IR spectra were taken in a neat film on a UR-20 spectrophotometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz and Tesla BS-497 spectrometer at 100 MHz in CCl₄, CDCl₃, and (CD₃)₂CO solution with HMDS internal standard. The mass spectra were taken on a MKh-13-03 spectrometer with 50 eV electron ionization energy and 200°C ionization temperature. The gas-liquid chromatography was performed on Chrom-4 chromatographs with SE-30 stationaryphase, 1.2 m column length, helium gas carrier, and 0.50-1 kg/cm² gas pressure and on a Chrom-42 chromatograph with 10% XC-2-1 stationary phase, 2.5 m column length, and 0.6-0.9 kg/mm² gas carrier pressure. The preparative product separation was carried out on a Tsvet 3-66 chromatograph with 10% XC-2-1 stationary phase, 2 m column length, nitrogen gas carrier, and 100-120 ml/sec gas flow rate.

General Method for the Reaction of Vinylsilanes with $CC1_4$ and $CHBr_3$. A sample of 1.25 mmole $(CH_2 = CHSiR_3) \cdot Fe(CO)_4$ complex, 50 mmole vinylsilane, and 50 mmole halomethane were added to a flask equipped with a reflux condenser in an argon atmosphere. The reaction mass was maintained for 4 h at 60-80°C and the precipitate was filtered off. The unreacted starting reagents were removed from the filtrate and the reaction products were separated by vacuum distillation.

The reaction of vinylsilanes with $CHCl_3$ was carried out in a titanium autoclave at $120^{\circ}C$ for 4 h on the π -complex with added TPP.

Reaction of Vinyltrimethylsilane with Halomethanes. The reaction of VTMS with CCl₄ yields a mixture of products consisting of 1,1,1,3-tetrachloro-3-trimethylsilylpropane (I), erythro- and threo-1,1,5-tetrachloro-3,5-bis(trimethylsilyl)pentanes (II) and (III) and erythro- and threo-1,1,5-trichloro-3,5-bis(trimethylsilyl)-1-pentenes (IV) and (V) in the ratio (I):(II):(III):(IV):(V) = 4.5:1:1:1.5:1.5. The products were identified by comparison with known samples [8].

1,1,3-Tribromo- (IX) and 1,1,3-trichloro-3-trimethylsilylpropane (XIII) were prepared in the reactions of VTMS with CHBr₃ and CHCl₃ and identified by comparison with known samples [8].

Reaction of Vinyltrimethoxysilane with CCl₄ and CHBr₃. Samples of 1,1,1,3-tetrachloro-3- (VI) and 1,1,3-tribromo-3-trimethoxysilylpropane (X) were obtained by the reaction of VTMOS with CCl₄ and CHBr₃ and identified by comparison with known samples [8].

A sample of 1,3-diviny1-1,1,3,3-tetramethoxydisiloxane (VII) was isolated with bp 65-66°C (7 mm), $n_D^{2^{\circ}}$ 1.4183 (see Bazant et al. [12], p. 209).

Reaction of Tetravinylsilane with CC1₄ and CHBr₃. A sample of tetrachloro-3-trivinylsilylpropane (VIII) was prepared with bp 99-100°C (2 mm), np^{2°} 1.4982. IR spectrum (ν , cm⁻¹): 545, 650, 670, 740-765, 830, 975, 1015, 1140, 1205, 1410, 1600, 3020, 3065. PMR spectrum (CC1₄, δ , ppm): 2.92-3.04 m (2H, C²), 3.47-3.72 m (1H, C³), 5.75-6.31 m (SiVin₃).

A sample of 1,1,3-tribromo-3-trivinylsilylpropane (XI) was prepared with bp 106-107°C (1 mm), np^{2°} 1.5462. IR spectrum (ν , cm⁻¹): 570, 590, 675, 745, 810, 910, 975, 1020, 1120, 1210, 1410, 1600, 3020, 3065. PMR spectrum (CDCl₃, δ , ppm): 2.53-2.80 m (2H, C²), 3.34-3.60 (1H, C³), 5.64-6.32 m (10H, SiVin₃, C¹). Double resonance was used to suppress the methylene protons at C² and permitted us to find that the methylene proton at C¹ is located at 5.84 ppm and has multiplicity J₁ = 8.5 and J₂ = 3.0 Hz.

Reaction of Divinyldimethylsilane with CHBr₃. A sample of 1,1,3-tribromo-3-vinyldimethylsilylpropane (XII) was prepared with bp 80-81°C (1 mm), np^{2°} 1.5311. IR spectrum (v, cm⁻¹): 550, 580, 665, 715, 795, 835-865, 910, 970, 1020, 1265, 1420, 1600, 3025, 3065. PMR spectrum (CDCl₃, δ , ppm): 0.21 s (6H, SiMe₂), 2.51-2.72 m (2H, C²), 3.24-3.44 m (1H, C³), 5.46-6.21 m (4H, SiVin, C¹). A double resonance experiment showed that the signal for the proton at C¹ is a multiplet at 5.75 ppm with J₁ = 8.5-9.0 and J₂ = 3.2-3.5 Hz. General Method for the Reaction of Vinyltrimethylsilane with Hydrosilanes on $(CH_2 = CHSiMe_3) \cdot Fe(CO)_4$ Complex. A sample of 1.0-2.0 mmoles π -complex, 40 mmoles VTMS, and 60 mmoles hydrosilane were loaded into a titanium autoclave previously flushed with argon and maintained for 3 h at 70-80°C. The unreacted starting compounds were removed from the mixture and the residue was distilled in vacuum.

A sample of 1-trichlorosily1-1-trimethy1sily1ethane (XIV) was isolated from the mixture of products obtained by the reaction of HSiCl₃ with VTMS by preparative gas chromatography with bp 88°C (32-33 mm). IR spectrum (ν , cm⁻¹): 470, 560, 590, 760, 790, 850-865, 1260, 2885, 2910, 2965. PMR spectrum (CDCl₃, δ , ppm): 0.12 s (9H, SiMe₃), 0.68 q (1H, CH), 1.21 d (3H, CH₃, J = 7 Hz). M⁺ 234 (mass spectrum). Product (XIV) was methylated using MeMgI in ether to yield 1,1-bis(trimethy1sily1)ethane (XXIV) with bp 59°C (27-28 mm), np^{2°} 1.4337 [13]. IR spectrum (ν , cm⁻¹): 700, 765-780, 840-875, 1010, 1115, 1260, 1430, 1465, 2840, 2880, 2920, 2965. PMR spectrum ((CD₃)₂CO, δ , ppm): -0.26 q (1H, CH, J = 7 Hz), -0.05 s (18H, 2SiMe₃), 0.96 d (3H, CH₃, J = 7.5 Hz).

A double resonance experiment to suppress the CH_3 group protons revealed that the methine proton at C¹ gives a quartet at -0.26. M⁺ 174 (mass spectrum).

The mixture of products (XIV)-(XVI) was methylated with MeMgI in ether. The methyl derivatives of (XIV)-(XVI) were identified by comparison with the pure compounds (XXIV), (XXV), and (XXVI).

A sample of 1-trichlorosily1-2-trimethy1sily1ethane (XV) was obtained by convergent synthesis by the method of Kanazashi [14] with bp 73-74°C (20 mm), np²⁰ 1.4470 [14].

A sample of 1,2-bis(trimethylsilyl)ethane (XXV) was synthesized by the methylation of (XV) using MeMgI in ether with bp 57-58°C (30 mm), $np^{2°}$ 1.4206 [15].

A sample of 1,2-bis(trimethylsilyl)ethylene (XXVI) was obtained by the reaction of VTMS with HSiMe₃ and separated by preparative gas chromatography with bp 48°C (15-16 mm), $n_D^{2^{\circ}}$ 1.4312 [16]. IR spectrum (v, cm⁻¹): 705, 725, 760, 845-865, 1020, 1180, 1255, 1415, 2910, 2940, 2965. PMR spectrum (CCl₄, δ , ppm): 0.05 s (18H, 2SiMe₃), 6.47 s (2H, CH=CH), M⁺ 172 (mass spectrum).

A sample of ethyltrimethylsilane (XVII) was prepared with bp 62°C (750 mm), np²⁰ 1.3824 (see Bazant et al. [12], p. 134).

A sample of 1-methyldichlorosilyl-1-trimethylsilylethane (XVIII) was prepared by the reaction of VTMS with HSiMeCl₂ and separated by preparative gas chromatography with bp 67°C (7-8 mm). IR spectrum (ν , cm⁻¹): 470-490, 540, 570, 760, 790, 810, 840-865, 995-1010, 1115, 1255-1265, 2885, 2910, 2965. PMR spectrum (CCl₄, δ , ppm): 0.07 s (9H, SiMe₃), 0.45 q (1H, CH), 0.67 s (3H, SiMe), 11.1 d (3H, CH₃, J = 7 Hz). M⁺ 214 (mass spectrum).

The mixture of products (XVIII)-(XX) was methylated and the methyl derivatives obtained were identified by comparison with pure samples of (XXIV)-(XXVI), respectively.

The products of the reaction of VTMS with $HSiMe_2Cl$ (XXI)-(XXIII) were not isolated as pure compounds and they were identified by chromatographic comparison of methyl derivatives (XXI)-(XXIII) with known samples of (XXIV)-(XXVI).

CONCLUSIONS

The high catalytic activity of $(CH_2=CHSiR_3) \cdot Fe(CO)_4$ complexes was demonstrated in the reaction of vinylsilanes with polyhalomethanes and hydrosilanes.

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REACTION OF VINYLGERMANIUMS WITH BUTADIENE

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There is no information in the literature on the cooligomerization of vinyl compounds of germanium with 1,3-dienes. However, this reaction opens new possibilities in the synthesis of polyalkenylgermaniums as shown in the case of vinylsilanes [1, 2].

In the present work, we studied the reaction of tetravinyl- and vinyltriethylgermanium with butadiene (BD) on nickel-containing catalytic systems. The use of a catalytic system containing NiCl₂, sesquialuminum chloride, and triphenylphosphine (TPP) in the reaction of BD with vinylgermanium leads to the formation of a mixture of hexadienyl germanium derivatives (I)-(IV) [3]

As in the case of hydrocarbon analogs [4], a slight change in the reaction conditions and catalytic system (NiCl₂ + Et₂AlCl + TPP in benzene) permits preparation of pure Δ^1 -Z-1,5-hexadienyl(trivinylgermanium) (V) in 48% yield

$$/ / + (/)_4 Ge \rightarrow / / / Ge (/)_3$$

IR, PMR, and UV spectroscopic methods showed that there are two unconjugated double bonds in (V). One of these double bonds is in a terminal position and the other is in the α -position to the germanium atom and has a Z-configuration (720 and 1600 cm⁻¹). We note that monoadducts with a different structure were obtained in the cooligomerization of trimethylvinylsilane with BD on the same catalytic system: 2-trimethylsilyl-E- and Z-1,4-hexadienes [5].

The cooligomerization proceeds somewhat differently on the catalytic system consisting of Ni(acac)2, TPP, and triethylaluminum (TEA). Butadiene reacts with tetravinyl- and vinyltriethylgermaniums to form mixtures consisting of two C_{10} isomers (VI) + (VII) and (VIII) + (IX) with total yields of 65 and 45%, respectively



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