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Catalysis of hydrosilylation

XXIII. * Effect of substituents at silicon on unusual hydrosilylation of vinylsilanes catalysed by nickel acetylacetonate

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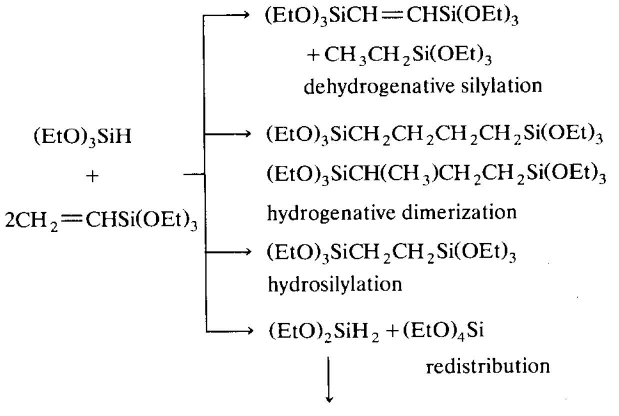
Abstract

Nickel acetylacetonate catalyses a competitive-consecutive reaction of trisubstituted silanes ($(EtO)_3SiH$ and Et_3SiH) with a variety of vinyl-trisubstituted silanes, giving products of dehydrogenative silylation, hydrosilylation and hydrogenative oligomerization as well as of disproportionation of substrates and dehydrogenative silylation of bis(silyl)ethenes. The conversion, yield and selectivities of the reaction have been influenced by many factors such as electronic and steric effects of the substituents at silicon of both initial substrates, as well as by the vinyl : hydrosilane ratio, the temperature and the presence of dioxygen.

1. Introduction

Dehydrogenative silylation competing with hydrosilylation of olefins has recently been the subject of extensive examinations. The former reaction proceeds in the presence of ruthenium, iron, rhodium, osmium, iridium and some platinum catalysts [1]. Contrary to the latter nickel complexes usually catalyse the hydrosilylation processes yielding predominantly a mixture of α and β adducts [2].

Our previous study on the reaction of vinyltriethoxysilane with triethoxysilane catalysed by nickel acetylacetonate ($Ni(acac)_2$) has shown the formation of bis(silyl)ethenes and bis(silyl)butanes formed by dehydrogenative silylation and hydrogenative dimerization of vinylsilanes respectively, accompanied by products of normal hydrosilylation and redistribution of hydrosilane, which can be summarized as follows [3]:



On the contrary, nickel complexes produced from nickel salts with alkylaluminium halides (and phosphines) have been found to be very active in the dimerization of vinylsilanes, *e.g.* trimethylvinylsilane [4,5], giving, in the

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* For Part XXII see ref. 12.

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absence of hydrosilanes, bis(silyl)butenes. Nickel acetylacetonate does not catalyse this reaction (the yield of dimers is less than 20% [4]).

The new competitive-consecutive reaction will be explained in this work mostly by the effect of substituents on silicon of both substrates.

2. Experimental details

2.1. Materials

Triethoxysilane, tetraethoxysilane, vinyltrimethoxysilane and vinyltripropoxysilane were obtained by alcoholysis of $\mathrm{SiHCl_3}$, $\mathrm{SiCl_4}$ and $\mathrm{CH_2{=}CHSiCl_3}$ respectively, according to the standard procedure.

Other chemicals were obtained from the following sources: vinyltriethoxysilane, vinyltrimethylsilane, vinyldimethylethoxysilane, triethylsilane and ethyltriethoxysilane from Fluka; vinyldiethoxyphenylsilane from ABCR; $\mathrm{Ni(acac)_2}$ and other catalysts from Pierce. All of these were used without futher purification. Bis(triethoxysilyl)ethane and bis(trimethylsilyl)ethene were obtained by metathesis of vinyltriethoxysilane and vinyltrimethylsilane, respectively, in the presence of $\mathrm{RuCl_2(PPh_3)_2}$ catalyst [6], and bis(triethoxysilyl)ethane by hydrosilylation of the respective vinylsilane catalysed by a standard Pt complex [2].

2.2. Equipment and analytical measurements

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian XL300 spectrometer (300 MHz; $\mathrm{CDCl_3}$). The mass spectra of products were determined by gas chromatography (GC)–mass spectrometry (MS) analysis (Varian 3300 gas chromatograph equipped with a DB-1, 30 m capillary column and a Finnigan Mat 700 ion trap detector). GC analysis was additionally performed on a Varian 3300 with Megabore Column DB-1, 30 m.

2.3. Hydrosilylation reaction (general procedure)

The catalyst ($\mathrm{Ni(acac)_2 \cdot 2H_2O}$ or $\mathrm{Ni(acac)_2}$) was placed in a glass ampoule (or in a flask equipped with a condensor) and filled with a mixture of vinyl-trisubstituted silane and trisubstituted silane ($\mathrm{HSi(OEt)_3}$ or $\mathrm{HSiEt_3}$). All manipulations were carried out using standard Schlenk and high vacuum-line techniques.

Sealed ampoules (or flasks) were heated at a given temperature (120°C) or under reflux (flasks). The distribution of substrates and product conversions of substrates and the yield of the reaction products were detected and calculated by GC–MS and GLC analysis.

2.4. GC–MS analysis of the products

These are given in the following format: [*m/z* (relative intensity, ion)]; retention time.

2.4.1. The reaction of triethoxysilane with vinyltriethoxysilane

$\mathrm{EtSi(OEt)_3}$ (**1**): [163 (100%, M − $\mathrm{C_2H_5}$), 147 (24%), 135 (14%), 119 (59%), 103 (19%), 91 (25%), 79 (43%), 63 (45%)]; 5.33 min.

$\mathrm{(EtO)_4Si}$ (**2**): [208 (20%, M), 193 (100%), 179 (22%), 163 (53%), 149 (75%), 135 (17%), 119 (28%), 107 (12%), 79 (26%), 3 (12%)]; 5.48 min.

$\mathrm{(EtO)_3SiCH{=}CHSi(OEt)_3}$ (**3**): [353 (100%, M + 1), 307 (31%), 293 (29%), 279 (49%), 251 (37%), 163 (10%), 119 (28%), 107 (16%), 79 (22%), 63 (20%)]; 14.01 min.

$\mathrm{(EtO)_3SiCH_2CH_2Si(OEt)_3}$ (**4**): [353 (1%, M − 1), 309 (100%), 281 (23%), 253 (12%), 163 (23%), 119 (20%), 79 (15%)]; 14.14 min.

$\mathrm{(EtO)_3SiCH(CH_3)CH_2CH_2Si(OEt)_3}$ (**5**): [382 (1%, M), 337 (57%), 307 (24%), 266 (39%), 263 (100%), 163 (58%), 119 (51%), 79 (38%), 63 (18%)]; 15.37 min.

$\mathrm{(EtO)_3Si(CH_2)_4Si(OEt)_3}$ (**6**): [381 (3%, M − 1), 337 (39%), 263 (100%), 163 (30%), 119 (18%), 79 (16%)]; 16.32 min.

$\mathrm{[(EtO)_3Si]_2C{=}CHSi(OEt)_3}$ (**7**): [469 (100%), 397 (14%), 323 (15%), 277 (10%), 91 (12%), 79 (18%)]; 17.48 min.

$\mathrm{[(EtO)_3Si]_2CHCH_2Si(OEt)_3}$ (**8**): [472 (24%), 471 (100%), 397 (15%), 279 (8%), 251 (9%), 119 (8%), 79 (4%)]; 17.53 min.

2.4.2. The reaction of triethoxysilane with vinyltripropoxysilane

$\mathrm{EtSi(OPr)_3}$ [235 (100%, M + 1), 205 (10%), 175 (10%), 147 (13%), 121 (22%), 105 (17%), 79 (29%), 59 (39%)].

$\mathrm{(EtO)_3SiCH{=}CHSi(OPr)_3}$: [395 (100%, M + 1), 307 (40%), 265 (30%), 163 (10%, 79 (18%)].

$\mathrm{(EtO)_3SiCH_2CH_2Si(OPr)_3}$: [396 (1%, M), 351 (45%), 337 (100%), 309 (5%), 267 (13%), 163 (4%), 119 (4%), 79 (6%)].

$\mathrm{(PrO)_3SiCH(CH_3)CH_2CH_2Si(OPr)_3}$: [466 (1%, M), 407 (100%), 365 (73%), 205 (10%), 163 (5%), 121 (15%), 79 (18%)].

$\mathrm{(PrO)_3Si(CH_2)_4Si(OPr)_3}$: [467 (3%, M + 1), 407 (15%), 365 (42%), 305 (100%), 205 (10%), 121 (19%), 79 (17%)].

2.4.3. The reaction of triethoxysilane with vinyltrimethoxysilane

$\mathrm{EtSi(OMe)_3}$: [151 (26%, M + 1), 121 (78%), 119 (100%), 91 (15%), 59 (32%)].

$\mathrm{(EtO)_3SiCH{=}CHSi(OMe)_3}$: [311 (22%, M + 1), 265 (100%), 163 (10%), 121 (24%), 91 (29%), 77 (20%)].

$\mathrm{(EtO)_3SiCH_2CH_2Si(OMe)_3}$: [312 (1%, M), 267 (100%), 251 (39%), 121 (28%), 91 (19%)].

$\mathrm{(MeO)_3Si(CH_2)_4Si(OMe)_3}$: [298 (1%, M), 267 (100%), 251 (20%), 121 (20%), 91 (9%)].

2.4.4. The reaction of triethoxysilane with vinyldimethylethoxysilane

EtSiMe$_2$(OEt): [133 (57%, M + 1), 117 (21%), 103 (100%), 87 (29%)].

(EtO)$_3$SiCH=CHSiMe$_2$(OEt): [293 (100%, M + 1), 292 (25%, M), 277 (53%), 248 (23%), 219 (30%), 103 (40%), 75 (17%)].

(EtO)$_3$SiCH$_2$CH$_2$SiMe$_2$(OEt): [294 (1%, M), 249 (100%), 221 (8%), 163 (5%), 103 (12%)].

(EtO)Me$_2$Si(CH$_2$)$_4$SiMe$_2$(OEt): [262 (1%, M), 247 (13%), 217 (100%), 103 (36%), 75 (12%)].

2.4.5. The reaction of triethoxysilane with vinyltrimethylsilane

EtSiMe$_3$: [103 (70%, M + 1), 87 (25%), 73 (100%), 72 (20%)].

(EtO)$_3$SiCH=CHSiMe$_3$ [263 (82%, M + 1), 247 (100%), 219 (22%), 163 (18%), 119 (22%), 73 (22%)].

Me$_3$SiCH=CHSiMe$_3$: [172 (5%, M), 157 (15%), 99 (12%), 73 (100%)].

(EtO)$_3$SiCH$_2$CH$_2$SiMe$_3$: [264 (5%, M), 249 (100%), 191 (23%), 163 (28%), 119 (22%), 73 (35%)].

Me$_3$Si(CH$_2$)$_4$SiMe$_3$: [202 (1%, M), 187 (3%), 99 (17%), 73 (100%)].

2.4.6. The reaction of triethoxysilane with vinylphenyldiethoxysilane

EtSiPh(OEt)$_2$: [225 (10%), M + 1), 195 (28%), 179 (100%), 165 (28%), 135 (52%), 121 (32%)].

(EtO)$_3$SiCH=CHSiPh(OEt)$_2$: [385 (2%), 341 (43%), 311 (32%), 253 (23%), 194 (22%), 163 (60%)].

(EtO)$_3$SiCH$_2$CH$_2$SiPh(OEt)$_2$: [385 (8%), 341 (18%), 324 (21%), 267 (20%), 223 (92%), 195 (70%), 145 (80%), 122 (100%)].

2.4.7. The reaction of triethylsilane with vinyltrimethylsilane

EtSiMe$_3$: [102 (3%, M), 87 (24%), 73 (100%), 59 (46%), 43 (12%)].

Et$_4$Si: [144 (5%, M), 115 (82%), 87 (100%), 59 (35%)].

Et$_3$SiOSiMe$_3$: [189 (8%), 175 (100%), 147 (68%), 119 (45%), 73 (15%), 66 (24%)].

Et$_3$SiCH=CHSiMe$_3$: [199 (19%), 185 (29%), 171 (29%), 157 (47%), 126 (23%), 101 (27%), 87 (49%), 73 (100%), 59 (80%).

Et$_3$SiCH$_2$CH$_2$SiMe$_3$: [201 (9%), 187 (60%), 159 (43%), 73 (100%), 59 (75%)].

Et$_3$SiOSiEt$_3$: [217 (100%), 189 (79%), 161 (46%), 133 (16%), 105 (19%), 80 (21%), 66 (24%), 59 (16%)].

Et$_3$SiCH=CHSiEt$_3$: [257 (13%, M + 1), 215 (17%), 199 (40%), 115 (93%), 87 (100%), 59 (94%)].

Et$_3$SiCH$_2$CH$_2$SiEt$_3$: [229 (29%), 217 (19%), 201 (34%), 175 (21%), 115 (100%), 87 (54%), 59 (83%)].

Tris(triethylsilyl)hexane: [429 (43%), 355 (100%), 281 (34%), 221 (23%), 147 (21%), 73 (89%)], at least five isomers.

2.4.8. The reaction of triethylsilane with vinyltriethoxysilane

Et$_3$SiCH=CHSi(OEt)$_3$: [305 (100%, M + 1), 275 (41%), 259 (47%), 163 (10%), 115 (17%)].

Et$_3$SiCH$_2$CH$_2$Si(OEt)$_3$: [305 (2%, M − 1), 277 (100%), 261 (12%), 203 (10%), 163 (8%), 115 (11%)]. Tris(triethylsilyl)hexane: [429 (43%), 355 (100%), 281 (34%), 221 (23%), 147 (21%), 73 (89%)] at least five isomers.

TABLE 1. Effect of oxygen and ratio of substrates on the hydrosilylation of vinyltriethoxysilane by triethoxysilane catalysed by Ni(acac)$_2$

Parameter (units)	Value				
	[CH$_2$=CHSi≡]:[HSi≡] 1:0.5		[CH$_2$=CHSi≡]:[HSi≡] 1:1		
	Air [a]	Ar [a]	Ar for 0.5 h	Ar for 1 h	Ar for 2 h
Conversion (%)					
HSi≡	100	100	73	90	97
CH$_2$=CHSi≡	94	98	100	100	100
Yield (%)					
CH$_3$CH$_2$Si≡	15	13	11	17	15
≡SiCH=CHSi≡	61	70	41	15	7
≡SiCH$_2$CH$_2$Si≡	3	Trace	15	25	30
≡SiCH(CH$_3$)CH$_2$CH$_2$Si≡	3	2	3	5	5
≡Si(CH$_2$)$_4$Si≡	10	15	21	21	23
(≡Si)$_2$C=CHSi≡	2	Trace	9	17	19
(≡Si)$_2$CHCH$_2$Si≡	Trace	–	–	–	–

Reflux; [CH$_2$=CHSi≡]:[Ni(acac)$_2$] = 1:5 × 10^{-3}; 2 h. [a]

3. Results and discussion

Previous stoichiometric examination on the reaction of triethoxysilane with vinyltriethoxysilane in the presence of Ni(acac)$_2$ [3] is now extended by GC–MS analysis which permits us to confirm the above-mentioned products (see sections 2.4.1–2.4.6) and characterize the rest of more highly bonded oligomers (products in sections 2.4.7 and 2.4.8). The latter are found to be a result of the consecutive reactions of bis(silyl)ethene with substrates, which proceed according to the following equations:

$$(EtO)_3SiCH{=}CHSi(OEt)_3 + HSi(OEt)_3 \longrightarrow [(EtO)_3Si]_2CH{-}CH_2Si(OEt)_3$$

$$2(EtO)_3SiCH{=}CHSi(OEt)_3 + HSi(OEt)_3 \longrightarrow [(EtO)_3Si]_2C{=}CHSi(OEt)_3 + (OEt)_3SiCH_2CH_2Si(OEt)_3$$

The increasing concentration of tris(silyl)ethene and the detection of tris(silyl)ethane in the products at higher relative concentrations of hydrosilane account for the decrease in the concentration of bis(silyl)ethene during the reaction (Table 1) as well as for the increase in β adduct and trissilylethane.

As we have seen, the hydrosilylation and dehydrogenative silylation of bis(silyl)ethene occur at a vinylsilane : hydrosilane ratio of almost 1 : 1, *i.e.* at relatively high concentrations of triethoxysilane and additionally under reflux, *i.e.* at higher temperatures (exceeding 150°C). If the reaction proceeds at 120°C, only small amounts of the trisilylethene are observed (Table 2).

In order to yield the maximum amount of bis(silyl)ethenes, specific conditions should be assured, *i.e.* double concentration of vinylsilane, high temperature (reflux) and an oxygen-and-moisture-free atmosphere. Under the required conditions, the redistribution of triethoxysilane observed previously [3] can be excluded. It is worth saying that a very high yield of bis(silyl)ethene in comparison with that of ethylsilane suggests that dehydrogenative silylation occurs not only via simultaneous hydrogenation of vinylsilane but also either via hydrogen or ethane evolution since, instead of ethylene, traces of ethane were detected in the gaseous products. Thus a metathetical conversion of vinylsilane can be excluded. The effect of substituents at silicon of vinylsilane on the reaction course at 120°C and distribution of products is summarized in Table 2. The MS and GC–MS spectral data of most products have been described in Section 2.4.

Apparently, the hydrosilylation of unsaturated product to give tris(silyl)ethene does not occur under such mild conditions for most substituents on silicon (except for vinyltriethoxysilane as mentioned before). The distribution of the reaction products and their yields are similar to those for the reaction with vinyltriethoxysilane.

Transition metal complexes are well known to catalyse readily the disproportionation of substituted silanes, which explains the occurrence of side reactions accompanying the hydrosilylation processes [7]. The hydrosilylation of vinyl-substituted silanes in the presence of platinum and other transition metal complexes also is accompanied by the exchange of the substituent at silicon of both initial substrates [8–10].

We have observed that nickel acetylacetonate catalyses a disproportionation of vinyl-trisubstituted silanes and of triethoxysilane, which results in the replacement of triethoxysilyl group of hydrosilane by Si(OPr)$_3$,

TABLE 2. Effect of substituents at silicon of vinylsilane on its reaction with triethoxysilane catalysed by Ni(acac)$_2$

Parameter (units)	Value for the following R$_3$					
	(OMe)$_3$	(OEt)$_3$	(OPr)$_3$	Me$_2$(OEt)	Me$_3$	Ph(OEt)$_2$
Conversion (%)						
HSi(OEt)$_3$	53	56	89	49	83	13
CH$_2$=CHSiR$_3$	85	100	94	61	70	23
Yield (%)						
CH$_3$CH$_2$SiR$_3$	20	12	7	13	7	Trace
(EtO)$_3$SiCH=CHSiR$_3$	36	48	14	26	37	11
(EtO)$_3$SiCH=CHSi(OEt)$_3$	–	–	12	3	4	–
R$_3$SiCH=CHSiR$_3$	–	–	–	–	7	–
(EtO)$_3$SiCH$_2$CH$_2$SiR$_3$	20	11	14	10	Trace	7
(EtO)$_3$SiCH$_2$CH$_2$Si(OEt)	–	–	12	–	–	
R$_3$SiCH(CH$_3$)CH$_2$CH$_2$SiR$_3$		2	12	–	–	–
R$_3$Si(CH$_2$)$_4$SiR$_3$	9	22	20	9	15	–
[(EtO)$_3$Si]$_2$C=CHSiR$_3$	–	4			–	–

[CH$_2$=CHSi≡]:[HSi≡]:[Ni(acac)$_2$] = 1 : 1 : 5 × 10^{-3}; ampoules; 120°C; 2 h.

$SiMe_2(OEt)$ and, especially, by $SiMe_3$ according to the following equation:

$$CH_2{=}CHSiR_3 + HSi(OEt)_3 \longrightarrow CH_2{=}CHSi(OEt)_3 + HSiR_3$$

Consequently, the following products of dehydrogenative silylation have been detected: $(EtO)_3SiCH{=}CHSi(OEt)_3$ and $R_3SiCH{=}CHSiR_3$ (Table 2).

Introduction of one phenyl group to vinylsilane gives rise to a drastic drop in the conversion and in the yields of products. The hydrosilylation of vinyldiphenylethoxysilane gave only traces of products, but no reaction between vinyltriphenylsilane and triethoxysilane under the conditions examined was observed.

Vinyl-chlorosubstituted silanes, *e.g.* $CH_2{=}CHSiCl_3$, $CH_2{=}CHMeSiCl_2$ and $CH_2{=}CHSiMe_2Cl$, do not undergo hydrosilylation at all (in the presence of $Ni(acac)_2$). Finally, we observed the formation of nickel chloride, which does not catalyse the reaction under the conditions studied. The formation of nickel chloride is due to migration of the chlorine atom from the silyl ligand to the metal followed by splitting of the M–Si bond, as was shown for chlorosilylruthenium hydrides [11].

Very interesting results on hydrosilylation were obtained by replacement of triethoxysilane by triethylsilane. Nickel acetylacetonate virtually catalyses not only dehydrogenative silylation and hydrosilylation of vinyltrimethylsilane and vinyltriethoxysilane respectively but also the preliminary exchange of silyl groups at both substrates followed by the dehydrogenative silylation, hydrosilylation and hydrogenative oligomerization (trimerization) of vinyltriethylsilane. The latter reaction observed for both initial vinylsilanes (trimethylvinylsilane and triethoxyvinylsilane) differs from the hydrogenative dimerization, which is characteristic of the triethoxysilane substrate. GC–MS analysis (see Section 2.4) shows several isomers of tris(triethylsilyl) hexanes. Semi quantitative results are presented in Table 3. The formation of trimethyltriethyldisiloxane as well as of hexaethyldisiloxane in the presence of traces of oxygen is evidence of the migration of silyl groups in the reaction system.

TABLE 3. Conversion of the substrates and the yield of products in hydrosilylation of vinyltrimethylsilane and vinyltriethoxysilane by triethylsilane catalysed by $Ni(acac)_2$

Paramets (units)	Value for the following R_3	
	Me_3	$(OEt)_3$
Conversion (%)		
$HSiEt_3$	92	37
$CH_2{=}CHSi{\equiv}$	100	42
Yield (%)		
$CH_3CH_2SiR_3$	8	3
$(C_2H_5)_4Si$	8	1
$Et_3SiOSiR_3$	4	2
$Et_3SiOSiEt_3$	3	–
$Et_3SiCH{=}CHSiR_3$	27	11
$Et_3SiCH{=}CHSiEt_3$	8	–
$Et_3SiCH_2CH_2SiR_3$	10	6
$Et_3SiCH_2CH_2SiEt_3$	3	–
$R_3Si(CH_2)_4SiR_3$	13	3
Tris(Triethylsilyl)hexane (five isomers)	13	16

$[CH_2{=}CHSi{\equiv}]:[HSi{\equiv}]:[Ni(acac)_2] = 1:1:5\times10^{-3}$; reflux; argon; 2 h.

4. Conclusions

(1) A complex course of the following competitive-consecutive reactions of trisubstituted silanes ($(EtO)_3SiH$ and Et_3SiH), with vinylsilanes, was observed in the presence of nickel acetylacetonate: dehydrogenative silylation given by

$$2CH_2{=}CHSiR_3 + HSi{\equiv} \longrightarrow {\equiv}SiCH{=}CHSiR_3 + CH_3CH_2SiR_3$$

hydrosilylation given by

$$CH_2{=}CHSiR_3 + HSi{\equiv} \longrightarrow {\equiv}SiCH_2CH_2SiR_3$$

hydrogenative oligomerization, *i.e.* dimerization (for $(EtO)_3SiH$) given by

$$3CH_2{=}CHSiR_3 + HSi{\equiv} \longrightarrow R_3SiCH_2CH_2CH_2CH_2SiR_3 + (R_3SiCH(CH_3)CH_2CH_2SiR_3) + {\equiv}SiCH{=}CHSiR_3$$

and trimerization (for Et_3SiH) preceded by the disproportionation, given by

$$CH_2{=}CHSiR_3 + Et_3SiH \longrightarrow CH_2{=}CHSiEt_3 + HSiR_3$$

$$4CH_2{=}CHSiEt_3 + HSiEt_3 \longrightarrow Et_3SiCH_2CH_2CH(SiEt_3)CH_2CH_2CH_2SiEt_3\ (+4\ \text{isomers}) + Et_3SiCH{=}CHSiEt_3$$

The main processes are accompanied by the following side reactions which under some conditions can be important: hydrosilylation and dehydrogenative silylation of unsaturated product given by

$$R_3SiCH{=}CHSi{\equiv} + HSi{\equiv} \longrightarrow R_3SiCH_2CH_2(Si{\equiv})_2$$

dehydrogenative silylation given by

$$CH_2{=}CHSiR_3 + HSi{\equiv} \longrightarrow R_3SiCH{=}CHSi{\equiv} + H_2$$

$$3CH_2{=}CHSiR_3 + HSi{\equiv} \longrightarrow R_3SiCH{=}CHSiR_3 + R_3SiCH{=}CHSi{\equiv} + CH_3CH_3$$

and disproportionation of substrates given by

$$CH_2{=}CHSiR_3 + HSi{\equiv} \longrightarrow CH_2{=}CHSi{\equiv} + HSiR_3$$

followed by some of the main reactions.

(2) The yield and selectivities of the complex reaction depends strongly on many factors, e.g. the vinylsilane : hydrosilane ratio, the temperature, the presence of O_2 as well as the electronic and steric effects of the substituents at silicon of both substrates.

(3) The yield of the reaction of triethoxysilane with $CH_2{=}CHSiR_3$ decreases essentially with an increase in electron donor properties and an increase in the steric hindrance of the substituents on the silicon of vinylsilane. No reaction with chloro- and triphenyl-substituted silanes is observed.

Acknowledgments

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