

Effect of Catalysts on the Reaction of Allyl Esters with Hydrosilanes

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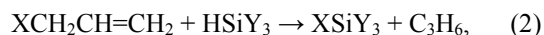
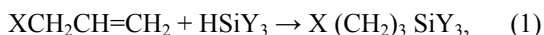
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Abstract—The reaction of hydrosilylation of allyl esters $\text{XOCH}_2\text{CH}=\text{CH}_2$ ($\text{X} = \text{MeCO}, \text{CF}_3\text{CO}, \text{C}_3\text{F}_7\text{CO}$) and $\text{PhOCH}_2\text{CH}=\text{CH}_2$ with hydrosilanes HSiY_3 ($\text{Y} = \text{Cl}, \text{OEt}$) in the presence of the Speier catalyst, the Speier catalyst with additives, and of various nickel complexes was studied. The catalytic hydrosilylation reaction in the presence of the Speier catalyst is accompanied by the reduction. Additives to the Speier catalyst (vinyltriethoxysilane and some ethers) allow to suppress considerably the reduction reaction. In the presence of the studied nickel complexes mainly reduction and isomerization reactions occurred. The best nickel catalysts of hydrosilylation were the mixtures of NiCl_2 or $\text{Ni}(\text{acac})_2$ with phosphine oxides. In contrast to allyl esters, the hydrosilylation of simple olefins proceeds easier, the content of the product of hydrosilylation in the reaction mixture reaches 94.3%.

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The reactions of hydrosilylation [Eq. (1)] of allyl esters in the presence of the Speier catalyst occurred with different yields (19–70%) [1–3] and often were accompanied with side reduction [Eq. (2)], and isomerization [Eq. (3)] reactions.



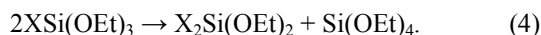
$\text{X} = \text{MeCOO}, \text{CF}_3\text{COO}, \text{C}_3\text{F}_7\text{COO}, \text{CH}_2=\text{C}(\text{CH}_3)\text{COO}, \text{Ph};$
 $\text{Y} = \text{Cl}, \text{OEt}.$

In this work we studied the influence of certain additives to the Speier and nickel catalysts on the course of the main and side reactions in the hydrosilylation of allyl esters and ethers.

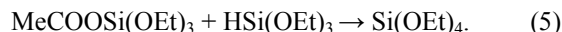
We showed that at the hydrosilylation of allyl acetate with triethoxysilane in the presence of the Speier catalyst with the addition of vinyltriethoxysilane the yield of acetoxypropyltriethoxysilane increased compared to the reaction without additives, from 84.3 to 88.7%, while the content of tetraethoxysilane fell from 8.8 to 0%. Tetraethoxysilane also is not formed when the hydrosilylation of allyl acetate was carried out in the presence of catalysts

formed at preliminary heating of the Speier catalyst with allyl acetate (Table 1). The absence of tetraethoxysilane in the product shows that reduction reaction is suppressed.

Tetraethoxysilane is formed from the product of reduction by disproportion.



At the hydrosilylation of allyl acetate the amount of tetraethoxysilane increases due to the reduction of acetoxy group in the acetoxytriethoxysilane.



Hydrosilylation of allyl phenyl ether in the presence of the Speier catalyst proceeded with the 70% yield [3]. Additives of vinyltriethoxysilane to the Speier catalyst significantly affect the reaction: the yield of γ -phenoxypropyltriethoxysilane increases up to 85% and the molar ratio of the addition product to the reduction product ADD/RED grows from 8.99 to 19.83 (Table 1). Similar situation is observed in the hydrosilylation of allyl methacrylate: adduct yield increases from 67 to 82%, and ADD/RED from 5.55 to 11.44%.

The process of hydrosilylation of allyl trifluoroacetate and allyl perfluorobutyrate was not affected by

Table 1. Hydrosilylation of $XCH_2CH=CH_2$ with hydrosilanes in the presence of various catalysts
 $XCH_2CH=CH_2 + HSiMe_nY_{3-n} \rightarrow X(CH_2)_3SiMe_nY_{3-n} + SiMe_nY_{4-n}$

X	Y	n	Catalyst [Concentration of Pt]	Conditions of synthesis			The composition of the mixture, %		ADD/ RED
				method	temperature, °C	time, h	$X(CH_2)_3SiMe_nY_{3-n}$	$SiMe_nY_{4-n}$	
CH ₃ COO	OEt	0	Speier catalyst [1×10 ⁻⁴]	2	Up to 100	2.0	84.3	8.8	7.57
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁶]	1	Up to 100	2.0	87.7	0	
			Speier catalyst + allyl acetate [2×10 ⁻⁶]	1	Up to 100	4.5	87.0	0	
			Speier catalyst + allyl trifluoroacetate [2×10 ⁻⁶]	1		0.5	88.8	0	
				1		0.5	9.7	0	
CF ₃ COO	Cl	0	Speier catalyst [2×10 ⁻⁴]	1		2.5	66.6	16.4	3.2
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁴]	2	80–90	0.5	86.6	1.4	
			Speier catalyst [2×10 ⁻⁴]	2		0.5	89.7	2.1	
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁴]	1		0.5	69.3	1.0	
			Speier catalyst [1×10 ⁻⁴]	1			68.1	1.0	
C ₃ F ₇ COO	OEt	0	Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁶]	2	65–100	10	42.5	26.0	1.06
			Speier catalyst + allyl acetate [2×10 ⁻⁶]	1		2	39.2	25.4	
			Speier catalyst [1×10 ⁻⁴]	1		2	38.0	26.0	
			Speier catalyst [1×10 ⁻⁴]	2	100–110	6	34.5	27.3	
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁴]	1.2			35.6	27.8	
CH ₂ =CMeCOO	OEt	0	Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁵]	2			37.8	27.0	0.7
			Speier catalyst [1×10 ⁻⁴]	2	50–100	1	67.0	8.7	
			Speier catalyst + vinyltriethoxysilane [1×10 ⁻⁴]	1	53–57	2	81.1	5.1	
			Speier catalyst + vinyltriethoxysilane [1×10 ⁻⁴]	2	50–100	1	74.5	6.2	
			Speier catalyst + vinyltriethoxysilane [1×10 ⁻⁴]	1	50–80	2.5	87.8	0.5	
PhO	OEt	0	Speier catalyst heated to 50°C [1×10 ⁻⁵]	3	70–100	2.5	82.2	6.4	8.99
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁴]	1	50–100	0.17	82.9	3.5	
			Speier catalyst + allyltriethoxysilane [1×10 ⁻⁵]	1	50–130	12	85.0	3.0	
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁶]	1		0.5	81.1	3.0	
			Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁶]	2	50	3	85	1.5	
Cl	Cl	0	Speier catalyst + vinyltriethoxysilane [2×10 ⁻⁶]	2	50–85	0.5	95.5	0	2.3
			Speier catalyst [1×10 ⁻⁴]	2	55–65	10	32.7	11.0	
			Speier catalyst + vinyltriethoxysilane [1×10 ⁻⁵]	2	50–80	3	89.2	5.3	
			Speier catalyst [1×10 ⁻⁴]	1	55–65	4	13.0	61.0	
			Speier catalyst + vinyltriethoxysilane [1×10 ⁻⁴]	1	55–65	4	22.7	50.1	

the addition of the vinyltriethoxysilane. This difference in the behavior of allyl trifluoroacetate and allyl perfluorobutyrate from allyl acetate is explained apparently by the difference in the ability of these reagents to the reaction of displacement of the vinyl ligand in the platinum-olefin complex. Trifluoroacetate addition to the Speier catalyst at the hydrosilylation of allyl acetate only reduces the reaction rate but does not exclude reduction.

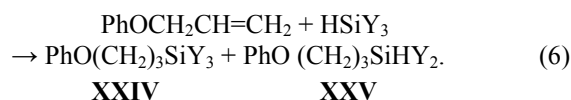
The rate of a reaction depends on the applied catalyst. It may be that the reduction reaction proceeds through the formation π -allyl complex of platinum whose formation is favored by the existence of ligand-acceptors [4]. We quantitatively characterized the increased role of reduction reaction depending on X by the molar ratio of product of addition and reduction ADD/RED. The following sequence was found: $\text{PhO} < \text{MeCOO} < \text{CH}_2=\text{C}(\text{Me})\text{COO} < \text{CF}_3\text{COO} < \text{C}_3\text{F}_7\text{COO} < \text{Cl}$.

This series coincides with the series of increase in the acidity of the residue X. Perhaps the suppression of formation of π -allylic complexes is due to the positive effects of amines [5] and amides [6] on the yield of the addition product at the hydrosilylation of allyl chloride in the presence of platinum catalysts. On the contrary, yield of γ -chloropropyltrichlorosilane at the hydrosilylation of allyl chloride with trichlorosilane using as a catalyst a solution of H_2PtCl_6 in allyl chloride is reduced by 15% compared to the Speier catalyst, probably due to the partial formation of π -allyl complexes. In the hydrosilylation of allyl chloride with triethoxysilane the ratio ADD/RED is particularly low (0.18). At the use of hydrochlorosilane instead of triethoxysilane the ADD/RED increases, and in the presence of the Speier catalyst with vinyltriethoxysilane it reaches 13.46. It should be noted that in the hydrosilylation of allyl acetate with triethoxysilane even in the presence of the Speier catalyst with vinyltriethoxysilane it was impossible to eliminate completely the reduction, but only possible to increase the ADD/RED ratio.

Nickel is known to form π -allyl complexes easier than platinum [7]. As catalysts for hydrosilylation of allyl phenyl ether with hydrosilanes we examined the following bivalent nickel complexes: $\text{NiCl}_2 \cdot (\text{PPh}_3)_2$ (**I**), $\text{NiCl}_2 \cdot [\text{P}(\text{C}_6\text{H}_{11})_3]_2$ (**II**), $\text{NiBr}_2 \cdot (\text{PBu}_3)_2$ (**III**), $\text{NiBr}_2 \cdot (\text{PPh}_3)_2$ (**IV**); zero-valence nickel complexes: $\text{Ni}(\text{CO})_2 \cdot (\text{PPh}_3)_2$ (**V**), $\text{Ni}(\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5) \cdot (\text{PPh}_3)_2$ (**VI**),

$\text{Ni}(1,5\text{-cod})_2$ (**VII**), $\text{Ni}(1,5\text{-cod}) \cdot (\text{DQ})^1$ (**VIII**), $\text{Ni}(\text{DQ})_2$ (**IX**), $\text{Ni}(\text{C}_{10}\text{H}_{12})^2 \cdot (\text{DQ})$ (**X**), $\text{Ni}(\text{TCC})_2^3$ (**XI**); hydride complexes: $\text{HNi}(\text{PPh}_3)_2\text{Br}$ (**XII**), $\text{HNi}[\text{P}(\text{C}_6\text{H}_{11})_3]_2\text{Br}$ (**XIII**); alkyl complex $\text{EtNi}[\text{P}(\text{C}_6\text{H}_{11})_3](\text{acac})$ (**XIV**), as well as some of these complexes and NiCl_2 (**XV**), $\text{Ni}(\text{acac})_2$ (**XVI**) mixed with the additives PPh_3 (**XVII**), CuCl (**XVIII**), and phosphine oxides $\text{Oct}_3\text{P}=\text{O}$ (**XIX**), $\text{MePh}_2\text{P}=\text{O}$ (**XX**), $\text{Bu}_2\text{PhP}=\text{O}$ (**XXI**), $\text{ClC}_6\text{H}_4\text{P}(\text{O})\text{Et}_2$ (**XXII**), $\text{HOC}_6\text{H}_4\text{P}(\text{O})\text{Et}_2$ (**XXIII**), forming complexes *in situ* (molar ratio complex : additive = 1:2).

Content of the adduct in the mixture formed after the reaction of hydrosilylation of allyl phenyl ether with triethoxysilane in the presence of the studied catalysts did not exceed 14.4% (**IX** + **XIX**), and in some cases along with the main product $\text{PhO}(\text{CH}_2)_3\text{SiX}_3$ (**XXIV**) formed hydrogenated compound $\text{PhO} \cdot (\text{CH}_2)_3\text{SiHX}_2$ (**XXV**), as is characteristic of nickel catalysts.



Similar data on the hydrosilylation of hexene with methyldichlorosilane were obtained by V.O. Reikhsfel'd and N.K. Skvortsov [8].

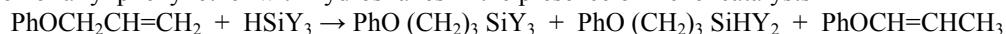
The content of the product of reduction $\text{C}_6\text{H}_5\text{OSiY}_3$ (**XXVI**) reached maximum 60% ($\text{Y} = \text{OEt}$) and 13.8% ($\text{Y} = \text{Cl}$), but the second product, namely propylene [Eq. (2)], and the products of hydrosilylation of the latter were not found. Perhaps, propylene underwent polymerization: in the synthesis always a dark-colored solid precipitate is formed, in some experiments in the GLC was detected a peak between the peaks of phenyltriethoxysilane and γ -phenoxypropyltriethoxysilane similar to that of propylene tetramer, that disappears at longer synthesis. The following sequence of activity in the reaction of reduction [Eq. (2)] is obtained (in parentheses the content of the reduction product in the reaction mixture, %): **XVI** + **XXIII** (60.6) > **XVI** + **XXI** (56.4) > **X** + **XIX** (55.3) > **X** + **XVII** (46.6) > **XVI** + **XXII** (46.2) > **XVI** + **XIX** (40.7) > **XI** + **XIX** (39.8) > **IX** + **XIX** (35.8) > **XV** + **XIX** (29.0)

The strongest reductive properties display nickel complexes containing as ligands duroquinone (**VIII**–**X**) and tetracyclone (**XI**) with phosphine oxides.

¹ DQ = duroquinone.

² $\text{C}_{10}\text{H}_{12}$ is bicyclopentadiene.

³ TCC is tetracyclone.

Table 2. Reaction of allyl phenyl ether with hydrosilanes in the presence of nickel catalysts

Catalyst	Molar ratio catalyst:allyl phenyl ether	Y	Conditions of reaction			The composition of the mixture, %			propylphenyl ether:allyl phenyl ether	Note
			method	temperature, °C	time, h	XXIV	XXV	XXVI		
I	10 ⁻³	OC ₂ H ₅	2	125	7	0	0	0		Solvent CH ₂ Cl ₂
	10 ⁻²	OC ₂ H ₅	2	125	20	0	0	8.3	15/32	
I + PPh₃	10 ⁻³	OC ₂ H ₅	2	140	20	0	0	29	21/15	
I + CuCl	10 ⁻³	OC ₂ H ₅	2	140	20	0	0	18	8.9/30	
II	10 ⁻³	OC ₂ H ₅	2	140	14	0	0	0	27/14	
	10 ⁻³	OC ₂ H ₅	1		20	0	0	0		
	10 ⁻³	Cl	1		20	0	0	0		
	10 ⁻²		1		25	0	0	0		
III	10 ⁻²	OC ₂ H ₅	1	115	25	4.7	0	21.1	5.6/14.5	Precipitate
IV	10 ⁻³	OC ₂ H ₅	2	145	17	0	0	18	19/10	
V		OC ₂ H ₅	1	125	24	Traces				
VI		OC ₂ H ₅	1	125	25	8.0	0	11	0	
VII		OC ₂ H ₅	1	135	20	0	0	0	0.08/1	
VIII		OC ₂ H ₅	2	150	14	0	0	0	1/16	
VIII + XIX	0.5×10 ⁻²	OC ₂ H ₅	1	115	25	12.0	1.5	60.3	3.8/9.3	Precipitate
IX	10 ⁻³	OC ₂ H ₅	1	110	70	0	0	16.7	0	
IX + XVII	10 ⁻³	OC ₂ H ₅	1	110	26	14.3	0.8	11.1	0	
IX + XIX		OC ₂ H ₅	1	115	26	14.4	0.8	35.8	3/9.2	Precipitate
X	10 ⁻³	OC ₂ H ₅	1		12	0	0	2.5		
X + XIX		OC ₂ H ₅	1	125	25	10.2	0	55.3	0/3.2	Precipitate
X + XVII	10 ⁻³	OC ₂ H ₅	1	125	12	5.6	0	46.6		Precipitate
XI		OC ₂ H ₅	1	125	25	0	0	0		
XI + XIX	10 ⁻³	OC ₂ H ₅	1	115	26	6.6	0.8	39.8	0	Precipitate
XII	10 ⁻³	OC ₂ H ₅	1	125	24	0	0	0	0	
XIII	10 ⁻³	OC ₂ H ₅	1	125	24	0	0	0	0	
XIV	10 ⁻³	OC ₂ H ₅	1	125	24	0	0	0	0	
X + XVII		Cl	1	125	25	7.1	0	16.4		
XV + XIX	1×10 ⁻³	Cl	1	125	25	78.2	1.2	2.4	0.23/0.3	Precipitate
	0.5×10 ⁻²	Cl	1	125	25	65.5	1.5			
XV + XX	1×10 ⁻²	Cl	1	125	25	19.2	19.4	12.2	5.0/3.0	
XV + XXI	1×10 ⁻²	Cl	1	125	25	35.6	7.9	13.8	3.1/2.0	
XV + XXII	1×10 ⁻²	Cl	1	125	25	20.2	10.3	9.9	6.0/6.6	
XV + XXIII	1×10 ⁻²	Cl	1	125	25	35.8	9.9	7.3	3.9/3.9	
XVI + XVII	1×10 ⁻²	Cl	1	125	25	10.7	3.8	10.5	20.2/21.4	
XVI + XIX	1×10 ⁻²	Cl	1	125	25	50.9	1.5	2.2	20.0/21.4	
		Cl	1	110	24	12.4		1.2	11.1/40.7	
XVI + XXI	1×10 ⁻²	Cl	1	125	25	69.0	3.3	3.9	5.8/1.6	
XVI + XXII	1×10 ⁻²	Cl	1	125	25	39.6	8.7	5.1	3.3/3.2	Gas
XVI + XXIII	1×10 ⁻²	Cl	1	125	25	32.5	8.3	9.7	9.3/6.0	Gas
XV + XIX	1×10 ⁻²	OC ₂ H ₅	1	125	25	11.2	2.5	29	1.3/5.1	Precipitate
XV + XX	1×10 ⁻²	OC ₂ H ₅	1	125	25	8.5	0.7	18.8	15.3/5.4	Precipitate
XVI + XVII	1×10 ⁻²	OC ₂ H ₅	1	125	25	0	0			
XVI + XIX	1×10 ⁻²	OC ₂ H ₅	1	125	25	10.7	6.2	40.7	1.3/1.6	Precipitate
XVI + XX	1×10 ⁻²	OC ₂ H ₅	1	125	25	8.5	0.7	11.8	15.3/15.4	
XVI + XXI	1×10 ⁻²	OC ₂ H ₅	1	125	25	5.7	1.5	56.4	0.9/4.4	Precipitate
XVI + XXII	1×10 ⁻²	OC ₂ H ₅	1	125	25	10.7	0.4	46.2	10.2/5.4	Precipitate
XVI + XXIII	1×10 ⁻²	OC ₂ H ₅	1	125	25	7.8	1.2	60.6	0.8/4.2	Precipitate

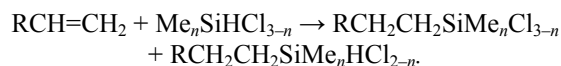
Table 3. Hydrosilylation of olefins with hydrochlorosilanes in the presence of nickel catalysts

Catalyst	R	n	Conditions of reaction			The composition of the mixture, %		Reaction (3) contribution, %
			method	time, h	temperature, °C	XXIV	XXV	
II	C ₆ H ₁₃	1	1	25	135	8.0	0	0
V	C ₅ H ₁₁	1	1	24	130	12.5	4.0	20
VI	C ₅ H ₁₁	1	1	25	125	21.0	14.3	0
VII	C ₅ H ₁₁	1	1	20	135	3.6	0	30
XII	C ₅ H ₁₁	1	1	25	125	0	0	0
XIII	C ₅ H ₁₁	1	1	24	125	17.5	3.6	0
XIV	C ₅ H ₁₁	1	2	25	125	8.0	0	0
XV + XIX	C ₅ H ₁₁	0	2	8	125	79.5	0	0
	C ₅ H ₁₁	0	2	5	125	70.3	0	0
	C ₆ H ₁₃	0	1	22	130	77.8	0	0
	C ₅ H ₁₁	0	1	22	130	94.3	0	0

Like with trichlorosilane, with triethoxysilane allyl-propenyl isomerization often occurred [Eq. (3)]. The ratio of the formed allyl propenyl ether to the initial allyl phenyl ether reaches even 3:1.

The degree of isomerization of allyl phenyl ether depends on the heating duration, the nature of the catalyst, and the concentration of the latter. Adding of copper(I) chloride and triphenylphosphine, two moles each relatively to the catalyst, increases dramatically the isomerization. It is also seen from the data in Table 2 that in the presence of triethoxysilane the contribution of isomerization is greater than in the presence of methyldichlorosilane and trichlorosilane. By special experiment we showed that in the absence of hydrosilane the isomerization of allyl phenyl ether under the same conditions does not occur. The isomerization occurs more often in the cases where no other reaction proceeds, but this is not the rule. In the presence of the other studied complexes the original substance returned unreacted.

The hydrosilylation of simple olefins in the presence of nickel catalysts proceeds easier and less complicated by the formation of by-products; the yield of the main compound reached 94.3% (Table 3).



EXPERIMENTAL

Products of reactions were analyzed on an LKhM-72 chromatograph equipped with a detector katharo-

meter, column 4×2000 mm, stationary phase Chromaton N-AW + 15% PMS 20000. The flow rate of carrier gas (helium) 60 ml min⁻¹. The temperature of the evaporator 550°C, of oven from 50 to 250°C, the programmed heating rate 20 deg min⁻¹. The substances obtained were identified by GLC by comparison with known samples.

Hydrosilylation in the presence of platinum catalysts. Speier catalyst (0.02 ml) + 0.02 ml of an additive was heated at 50°C for 0.5 h, then 0.1 mol of hydrosilane was added and over 20–25 min 0.1 mol of allyl ester (or allyl chloride) was added at 50–65°C (without heating). Then heating was continued for some time (*method 1*). *Method 2*: the order of addition is reversed. *Method 3*: the components were added as a mixture.

Hydrosilylation in the presence of nickel catalysts. To the reaction vessel flushed with argon were placed 0.01 mol of allyl phenyl ether, 0.015 mol of hydrosilane and the catalyst. The mixture of reactants with the catalyst was refluxed in the flask (*method 1*). The ampoule with the components was sealed and heated at a certain temperature (*method 2*).

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