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Continuous and Batch Organomagnesium Synthesis of Ethyl-Substituted Silanes from Ethylchloride, Tetraethoxysilane, and Organotrichlorosilane for Production of Polyethylsiloxane Liquids. 2. Continuous One-Step Synthesis of Ethylethoxy- and Ethylchlorosilanes

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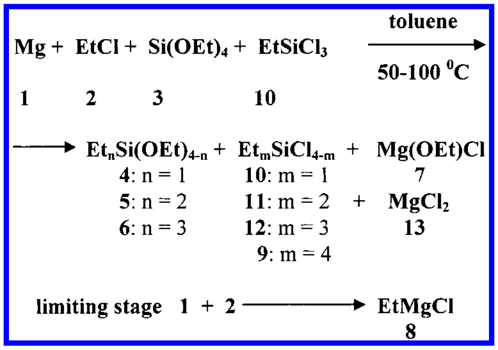
Abstract:

Development of a continuous one-step manufacturing process for ethylethoxy- and ethylchlorosilanes is described. The methodology of synthesis of ethyl-substituted silanes has been improved. The important factors for the successful synthesis have been determined. Among them are (1) the replacement of some tetraethoxysilane 3 by ethyltrichlorosilane 10, (2) the optimum concentration of 3 and 10, (3) the excess of the granulated magnesium (the supply rate 50−110 g h^{-1}), and, finally, (4) the columnar apparatus with the stirrer, resulting in high yields of di- and triethylsilanes, low duration of synthesis, and high selectivity of Grignard reagent. Continuous one-step synthesis has been assimilated into industry (up to a scale 7−40 kg h^{-1} of magnesium) for production of oligoethylsiloxanes with low (5−20%) and high content (up to 40%) of the terminal triethylsiloxy groups. The rules for R/D process of the Grignard synthesis are described.

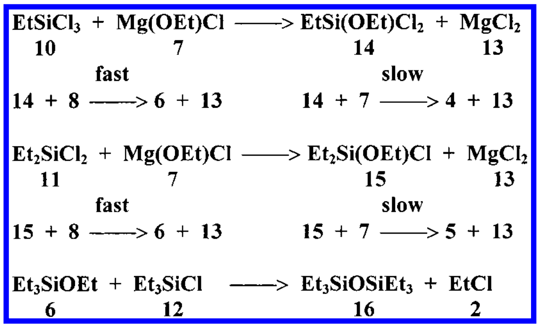
Introduction

In the preceding paper[1] we have improved the methodology of the batch one-step synthesis of ethyl-substituted silanes[1−4] through the use of tetraethoxy-**3** and chlorosilanes as reagents (Schemes 1, 2). Previous routine methods for the synthesis of ethylethoxysilanes[5−11] (Scheme 3) or of ethylchlorosilanes[12−19] (Scheme 4), which exploited as reagents either ethoxy- or chlorosilanes gave low yields of

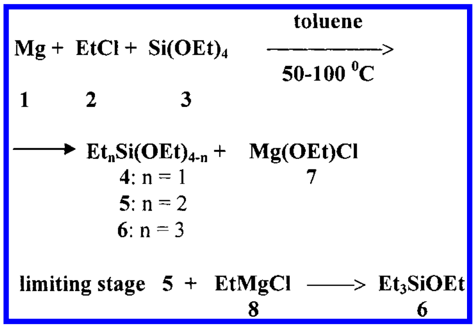
Scheme 1. **One-step organomagnesium synthesis of ethyl-substituted silanes**



Scheme 2. **Side processes of synthesis of ethyl-substituted silanes**



Scheme 3. **One-step organomagnesium synthesis of ethylethoxysilanes**



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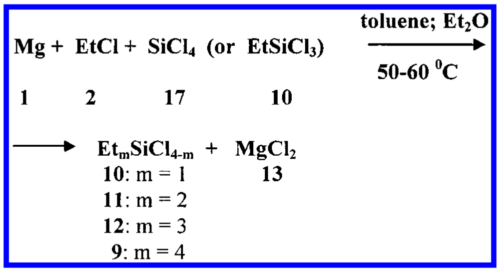
Scheme 4. **One-step organomagnesium synthesis of ethylchlorosilanes**



triethylsilanes, low conversion of Grignard reagent, and high duration of synthesis. We have determined important factors for a successful synthesis. Among them are (1) the replacement of some ethoxysilane **3** by chlorosilane **10**, resulting in high yields of triethylsilanes and low duration of synthesis due to replacement of the limiting stage of synthesis, (2) the optimum concentration of **3** and **10**, resulting in a high selectivity of Grignard reagent due to agreement between the rate of formation of Grignard reagent and the rate of formation of ethylsilanes.

The best results were obtained at mole ratio **2**:**3** = 2.6−3.3 (the lack of **3** and high yields (30−63%) of triethyl-substituted silanes **6** + **12** + **16**). The worst results were obtained at mole ratio **2**:**3** = 2.0−2.2 (the presence of silane **3** and high yields (16−23%) of monoethylsilanes **4** and **10**).

Because of this, the batch one-step synthesis has been assimilated into industry (up to a scale 240 kg of **1**)[1,20] only for production of oligoethylsiloxanes with the high content (up to 40%) of the terminal triethylsiloxy groups.

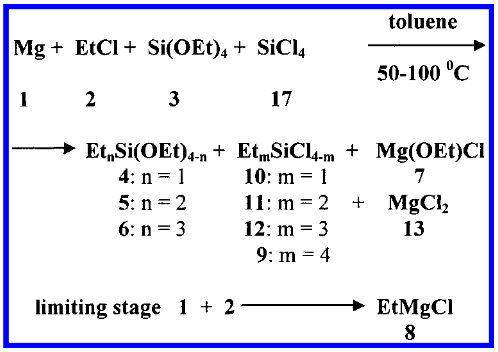
The disadvantages of this batch process are high contents of **3**,**4** and **10** in reaction products by mole ratio **2**:**3** = 2.0−2.4 and low capacity of reactors.

The goal of this study was to improve the process further.

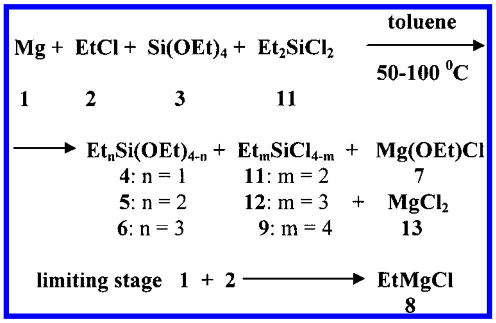
Results and Discussion

On the basis of our investigation of the continuous one-step organomagnesium synthesis of ethyl-substituted silanes from ethoxysilane **3** and tetrachlorosilane **17** (Scheme 5)[12,21] and from **3** and diethylsilane **11** (Scheme 6)[22,23] and on the basis of our investigation of the impact of magnesium on continuous one-step synthesis of organo-substituted silanes,[24−32] we reasoned that the development of the continuous synthesis (Schemes 1, 2) and the using of MG-90 magnesium[33−36] with a needle size of 1 × 4−12 mm, obtained by granulation of magnesium melt in strong magnetic fields[37,38] could improve this process (Schemes 1, 2) and the processes (Schemes 5, 6).

Scheme 5. **One-step organomagnesium synthesis of ethyl-substituted silanes**



Scheme 6. **One-step organomagnesium synthesis of ethyl-substituted silanes**



We will discuss the main results obtained by changing the ratio of the reactants, **3** and **10**, and by using magnesium MG-90 under conditions of continuous synthesis.

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Table 1. **Effect of concentration of 3 and 10 on composition of ethylsilanes and the conversion (C) of 8 in continuous one-step processes**[a]

	M			yield[b] (%) for compounds listed in Scheme 1								C (%)
entry	**3**	**10**	**2/3**	**3**	**4**	**5**	**6**	**10**	**11**	**12**	**9**	**8**
Syntheses of Ethylethoxysilanes[c] (magnesium L-29)												
1	1.360	0.000	2.2	0.0	9.0	89.0	2.0	0.0	0.0	0.0	0.0	88.0
2	1.250	0.000	2.4	0.0	0.0	97.0	3.0	0.0	0.0	0.0	0.0	85.0
Syntheses of Ethylethoxysilanes and Ethylchlorosilanes (magnesium L-29)												
3	1.090	0.500	2.2	0.0	5.7	63.3	17.9	3.5	9.4	0.2	0.0	93.9
4a	1.000	0.820	2.1	0.2	7.6	46.1	17.4	12.4	14.7	1.6	0.0	94.3
4b	0.960	0.750	2.2	0.0	4.3	49.8	18.4	10.9	15.6	1.0	0.0	92.2
5	0.860	1.080	2.0	1.0	3.9	37.4	20.0	10.9	24.9	1.9	0.0	94.7
6	0.842	1.010	2.1	0.0	0.0	39.4	20.7	8.4	28.8	2.7	0.0	96.3
Synthesis of Ethylethoxysilanes and Ethylchlorosilanes (magnesium MG-90)												
7	0.694	0.750	2.6	0.0	0.0	39.5	27.5	1.0	22.5	8.5	1.0	91.9

[a] [EtCl] = 3.000 M; temperature 50−100 °C. [b] Deviation from the average values was within ±1.5% abs. (for 20% and higher content of components). [c] For comparison.

Table 2. **Ethyltrichlorosilane 10 conversion in the continuous one-step synthesis of mixture of ethylethoxysilanes and ethylchlorosilanes**

amount [mol (%)] of **10**		yield [mol (%)] of conversion product			amount of **7** consumed in **10** ethoxylation
initial	final	**11**	**12**	**6**	
0.500	0.058 (11.6)	0.166 (33.1)	0.002 (0.4)	0.274 (54.8)	11.4
0.750	0.192 (25.5)	0.288 (38.4)	0.020 (2.7)	0.250 (33.3)	11.4
1.080	0.216 (20.0)	0.513 (47.5)	0.042 (3.9)	0.309 (28.6)	15.2
1.010	0.156 (15.4)	0.559 (55.3)	0.055 (5.5)	0.240 (23.8)	11.5
0.750	0.014 (1.9)	0.338 (45.0)	0.135 (18.0)	0.263 (35.1)	15.0

Effect of the Concentration of 3 and 10 on the Composition of 4−6 and 9−12 and on the Conversion of 8 and 1. First, we investigated this effect more closely than was in the case of the batch process.

Continuous syntheses were performed with the excess of granulated magnesium L-29[26,32] (granules 1−3 mm; Table 1, entries 1−6) and magnesium MG-90[37,38] (Table 1, entry 7) in the columnar dispersed plug flow reactors (Figure 1a/entries 1, 2, 5, and 6; Figure 1b/entries 3, 4 and Figure 1c/entry 7) with a countercurrent mode relative to liquid reagents.

The experimental results (Table 1) show that yields of triethylsilanes **6** and **12** and ethylmagnesium chloride **8** conversion in the continuous one-step synthesis of ethylsilanes (Schemes 1, 2) are greater when the initial mixture contains ethyltrichlorosilane **10** (entries 3−7).

These results also show that the relative content of ethylchlorosilanes **10**, **11** in the product mixtures is much lower than relative content of ethyltrichlorosilane **10** in the starting mixtures.

An increase in triethylsilane **6** in the product (Table 1) and low yields of chlorosilanes are explained by reactions (Scheme 2).

As follows from the preceding paper,[1] this is due to ethoxylation of ethylchlorosilanes **10**, **11** with ethoxymagnesium chloride **7** and ethylation with Grignard reagent **8**.

The relative content of silane **6** (Tables 1 and 2) show that the rates of these reactions (Scheme 2) are higher by a factor of 10 than the rate of silane **5** alkylation by **8**.

The rates of these reactions (Scheme 2) are also higher than the rate of diethyldichlorosilane **12** alkylation by **8**.

Scheme 2 explains the increase in the content of silane **6** in the product with increasing concentration of **10** in the reagent mixture since the reactivity of silanes increases in the order ethoxysilanes < chlorosilanes < ethoxy(chloro)-silanes.[39,40]

However, under conditions of continuous synthesis (the minimum quantity of catalyst **3**:**2** = 0.23−0.36; plug flow reactor), this order of reactivity is somewhat different.

The fact that the reaction products contain practically no ethoxysilane **3** and a low amount of ethoxysilane **4** indicates relatively high rates of ethylethoxysilanes **4** and **5** formation; a high chlorosilane **10** content suggests a rather low rate of chlorosilane **11** formation.

Therefore, under conditions of one-step continuous synthesis, the reactivity of ethoxysilanes **3** and **4** (catalysts of

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(38) A distinguishing feature of this magnesium is a lesser size of its crystallite grains (by a factor of 2−10). The size of the dendritic parameter and the subdendritic grain in granules produced from magnesium alloys can be changed within the limits of 2−10 μm.

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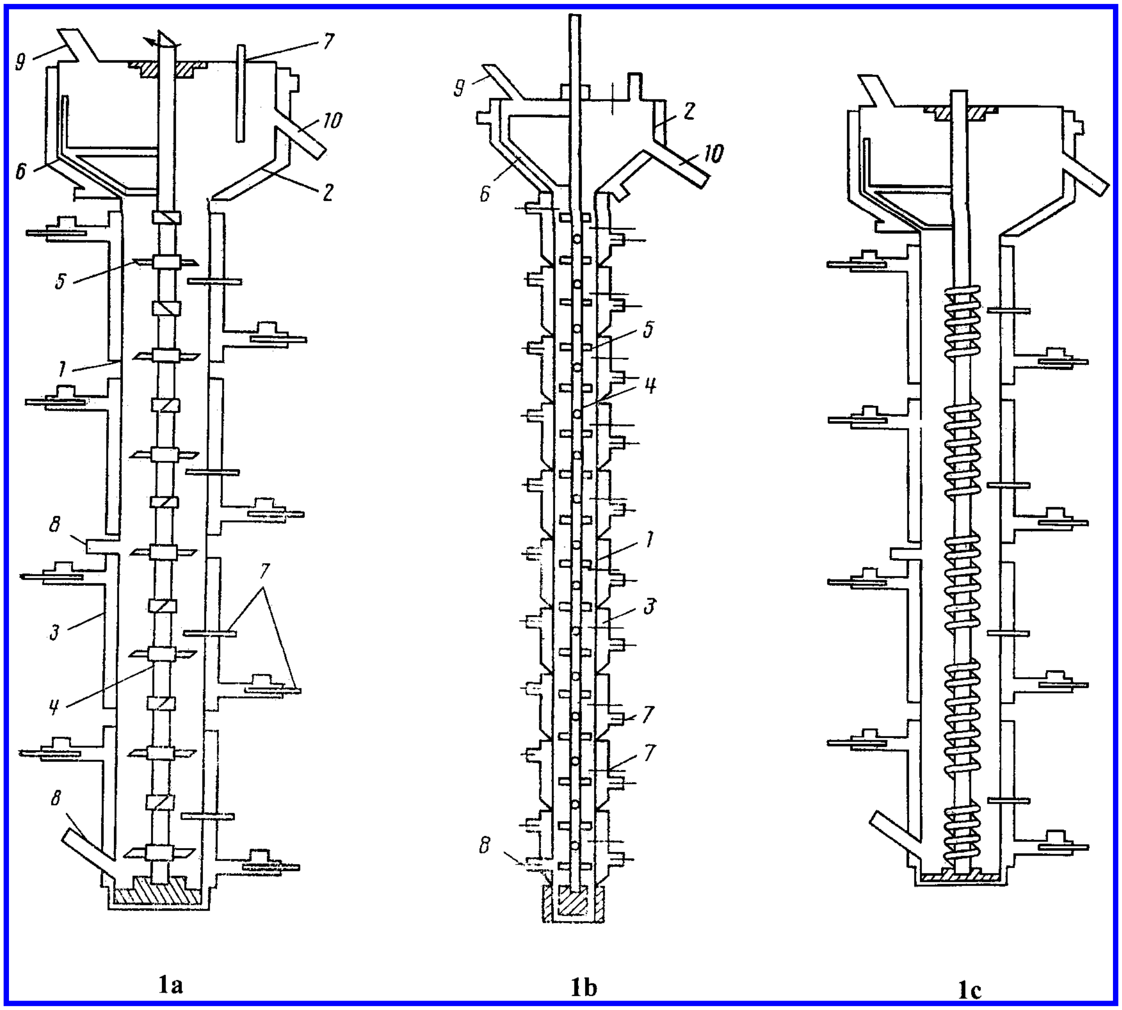

Figure 1. **Columnar dispersed plug flow reactors (CDPFR):[12,21,26,27,47] (1) reactor body; (2) separator; (3) cooling jacket; (4) stirrer; (5) paddle; (6) frame; (7) thermocouple pocket; (8) connecting pipe for mixture input; (9) connecting pipe for magnesium input; (10) connecting pipe for product removal.**

Grignard reagent **8** formation) toward ethylmagnesium chloride **8** is higher than that of chlorosilane **10** for the minimum quantity of catalyst (molar ratio **3**:**2** = 0.23−0.36). It is likely that this effect stems form formation of complexes of **8** with **3** and **4**.[41,42]

Note, that although the reaction products contain large amounts of **7** and **10**, not more than 15% of **7** is involved in the reaction (Table 2).

The lack of ethyl chloride **2** in the reaction products and in the gaseous phase in the reactor separator (Table 3) indicates its complete conversion. These data (Table 3) show that among side reactions accompanying Grignard reagent **8** formation, hydrogen abstraction from the solvent molecules is predominant.

Small quantities of Grignard reagent **8** (0.2−2.0%) and magnesium **1** (0.14−1.40%) are swept away by the reaction products (Table 4, entries 3−6).

The yield of Grignard reagent **8** reaches 98.3% (Table 1, entry 6).

Therefore, the procedure developed in this work allows us to control the composition of the reaction products for production of oligoethylsiloxanes both with the high and low contents of the terminal triethylsiloxy groups, and conversion of the initial reagents and intermediates is almost complete.

Table 3. **Composition of the gas phase in the separator of the reactor**

	gas content (vol. %)			
component	entry 3	entry 4	entry 6	entry 7
ethylene	5.9−9.2	6.2−7.1	5.3−8.3	5.2−5.3
ethane	57.1−79.3	67.9−75.1	39.9−54.3	60.9−61.1
X[a]	2.8−10.1	0.0−14.4	0.0	0.0
butane	2.4−7.6	1.6−3.8	10.3−15.8	8.6
2	0.0	0.0	0.0	0.0−0.5
toluene	6.8−23.6	7.7−16.2	22.2−44.5	25.1−26.2

[a] Unidentified component.

Note, that the residence time of the reaction mixture with magnesium is just 6−20 min.

Three advantages of continuous synthesis, (1) the best product distribution, (2) lack of tetraethoxysilane **3** in the product, and (3) the higher conversion of ethylmagnesium chloride, are discussed in following section.

Effect of Synthesis Method and of Reactor Type, and of Magnesium Excess. It is well-known that synthesis

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Table 4. **Content of Grignard reagent 8 and magnesium 1 in the product**[a]

duration of synthesis (h)	content (%) of **8** entry 3	entry 4	entry 5	entry 6	entry 7	content (%) of **1** entry 3	entry 4	entry 5	entry 7
1	0.18	0.07	0.11	0.35	0.26	0.01	0.11	0.01	0.01
2	0.17	0.06	0.14	0.37	0.42	0.03	0.01	0.03	0.01
3	0.23	0.07	0.16	0.43	0.79	0.06	0.09	0.07	0.02
4	0.08	0.08	0.17	0.42	0.98	0.04	0.01	0.07	0.02
5	0.10	0.09	0.15	0.42	1.40	0.08	0.09	0.07	0.03
6	0.09	0.09	0.10	0.50	0.29	0.15	0.08	0.05	0.03
7	0.04	0.07	0.12	0.45	*b*	0.10	0.07	0.06	0.03

[a] 0.10% content of Grignard reagent **8** or magnesium **1** in the resulting product corresponds to 0.38% of the theoretical amount of **8** or to 1.37% of the loaded amount of **1**. [b] Not determined.

Table 5. **Effect of synthesis method (SM)/batch (B) or continuous (C)/ and of reactor type (RT)/well-stirred reactor (WSR)[1] or columnar dispersed plug flow reactor (CDPFR)[12,21,26,27,47]/ on ethylsilane composition and conversion (C) of 8 in one-step processes**[a]

SM	RT	M **3**	**10**	**2/3**	yields (%) for compounds listed in Scheme 1 **3**	**4 + 10**	**5 + 11**	**6+12+16**	C (%) **8**
B[b]	WSR	1.040	0.464	2.3	7.7	15.1	53.8	23.4	84.5
B[b]	WSR	0.910	0.696	2.3	7.0	15.9	49.5	27.6	85.9
B[b]	WSR	0.786	0.928	2.3	3.3	9.2	58.4	29.1	92.8
C[c]	CDPFR(1b)	1.090	0.500	2.2	0.0	9.2	72.7	18.1	93.9
C[c]	CDPFR(1b)	0.960	0.750	2.2	0.0	15.2	65.4	19.4	92.2
C[c]	CDPFR(1a)	0.860	1.080	2.1	0.0	8.4	68.2	23.4	94.7

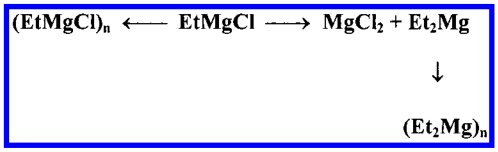
[a] [EtCl] = 3.000 M; temperature 50−100 °C. [b] Entries 3−5 (Table 1) preceding paper.[1] [c] Entries 3−5 (Table 1).

method (batch or continuous) and reactor type (well-stirred or columnar plug flow) determine the product distribution for the high-rate consecutive competitive reactions.[43] The continuous process and columnar plug flow reactor ensure a higher yield of intermediate products.[43]

It is also known[12,21,44,45] that synthesis method (batch or continuous) and reactor type (well-stirred or columnar plug flow) determine the product distribution for the reactions of ethylmagnesium chloride with the mixture of tetraethoxy- and tetrachlorosilane (Scheme 5), or only with tetrachlorosilane (Scheme 4). The continuous method and columnar plug flow reactors (Figure 1a, 1b, and 1c) ensure higher yields of diethylsilanes (**5**, **11**), lower yields of ethylsilanes (**4**, **10**) and triethylsilanes (**6**, **12**, **16**), and lack of **3**.[12,21,44,45]

This being the case, we investigated this effect for the reaction of ethylmagnesium chloride with the mixture of tetraethoxy- and ethyltrichlorosilane (Scheme 1).

Scheme 7. **Processes lowering reactivity of ethylmagnesium chloride 8**



$$\begin{array}{l} (EtMgCl)_n \longleftarrow EtMgCl \longrightarrow MgCl_2 + Et_2Mg \\ \hspace{9em}\downarrow \\ \hspace{8.5em}(Et_2Mg)_n \end{array}$$

As we might expect, the continuous one-step method (Scheme 1) and columnar dispersed plug flow reactors (Figure 1a, 1b, and 1c) also ensure (1) higher yields of diethylsilanes (**5**, **11**), lower yields of ethylsilanes (**4**, **10**) and triethylsilanes (**6**, **12**, **16**), and lack of **3** (Table 5). The continuous process also ensures (2) higher conversion of Grignard reagent **8** (Table 5). In addition, it is significant that (3) conversion of Grignard reagent **8** increases with increasing concentration of ethyltrichlorosilane **10** (Table 1, entries 3−6).

Result (1) shows that macrokinetics of continuous one-step process (Scheme 1) is consistent with the theoretical model of macrokinetics for the high-rate consecutive competitive reactions in columnar plug flow reactors.[43]

Results (2) and (3) show that processes lowering reactivity of Grignard reagent **8** (Scheme 7) are of little consequence.

There is no doubt that the excess of the granulated magnesium particles plays the role of the grinding balls in reactors. The stirred column apparatus with magnesium works as a mill. The formation of finely divided Grignard reagent **8** adds to the extent to which the reaction proceeds (from 84 to 85% in batch process to 92−96% in continuous process).

This is due to higher reactivity of the finely divided Grignard reagent **8** particles.

The results of our investigations[24−32] of the various grades of magnesium with size of particles from 600 μm[24] to 3 cm[27] add considerable support for the view of the stirred column

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(43) Levenspiel, O. *Chemical Reaction Engineering;* Wiley and Sons: New York, London, 1965; Chapters 7, 12.

(44) Klokov, B. A.; Sobolevskii, M. V.; Sakhiev, A. C.; Grishutin, Ju. P.; Bezlepkina, V. M. Organomagnesium Synthesis of Ethyl-substituted Organosilicon Monomers. VIII. Improved Laboratory Apparatus for Continuous Organomagnesium Synthesis. Methodology and Scientific Aspects of Continuous Organomagnesium Synthesis of Ethylchlorosilanes [in Russian]; No. 1006-khp-D-84. Filed at ONIITEKhIM, Cherkassy, October 31, 1984.

(45) Kalliopin, L. E.; Simanenko, E. A.; Sakhiev, A. C.; Sobolevskii, M. V.; Vavilov, V. V.; Gerlivanov, V. G.; Klokov, B. A. Organomagnesium Synthesis of Ethyl-substituted Organosilicon Monomers. V. Continuous Synthesis of Ethylethoxysilanes [in Russian]. No. 127-khp-D-84. Filed at ONIITEKhIM, Cherkassy, February 6, 1984.

apparatus with magnesium as the mill and of the granulated magnesium as grinding balls. The types of magnesium with size of particles from 600 μm to 0.1 cm are unsuitable for continuous syntheses of organo-substituted silanes. In this case the magnesium particles do not work as grinding balls.

Effect of Magnesium Type. Various grades of magnesium were tested. The results (Table 1, entries 1−6; Table 4, entries 3−6) show that the use of granulated magnesium L-29[12,28] (entries 1−6) makes it possible to obtain a product with a high selectivity of the Grignard reagent **8** (up to 96.3%). A small amount of magnesium (0.14−1.40%) is carried away by the synthesis products (Table 4).

The results (entry 7, Table 1) show that the use of magnesium MG-90 results in high yield of triethylsilanes **6** and **12** because of its high reactivity caused by small grain size.

However, during the first hours of the synthesis magnesium MG-90 grinds the Grignard reagent to a lesser extent due to a lower grain density (entry 7, Table 4). This causes the increase in the content of Grignard reagent in the product. Then, by the sixth hour of the reaction, the magnesium MG-90 grain density grows, and the Grignard content in the product drops.

Thus, magnesium L-29 and magnesium MG-90 are well-suited for continuous syntheses of ethylsilanes.

Continuous Synthesis on an Industrial Scale. A continuous process has been assimilated into industry (up to a scale 7−40 kg h^{-1} of magnesium) for the production of oligoethylsiloxanes with low (5−20%) content of the terminal triethylsiloxy groups from the reaction products prepared with the use of low (up to 0.500 mol L^{-1}) concentration of ethylsilane **10** and with the use of granulated magnesium (the size of the magnesium grain is 3−20 mm) in 1982.

In 1996 a continuous process was assimilated into industry with the use of magnesium obtained by granulation of a magnesium melt in strong magnetic fields (the size of the magnesium grain is 3−20 mm).[46]

Continuous synthesis on an industrial scale (in 1982) will be dealt with separately in our next publication.

The main results of this work were patented.[20,27,36]

Conclusions

We have improved the technology and the methodology of the synthesis of ethyl-substituted silanes. Previous routine methods (synthesis of ethylchlorosilanes or of ethylethoxysilanes), which exploited as reagents chloro- or ethoxysilanes, gave low yields of triethylsilanes, low conversion of Grignard reagent, and high duration of synthesis.

We have determined important factors for a successful synthesis. Among them are (1) replacement of some ethoxysilane **3** by chlorosilane **10**, resulting in high yields of triethylsilanes and low duration of synthesis due to replacement of the limiting stage of synthesis, (2) the optimum concentration of **3** and **10**, resulting in high selectivity of Grignard reagent due to agreement between the rate of formation of Grignard reagent and the rate of formation of ethylsilanes, (3) the excess of the granulated magnesium as a grinding balls, and (4) the columnar apparatus with the stirrer as a mill, resulting in higher selectivity of Grignard reagent and high yields diethylsilanes or triethylsilanes.

Continuous one-step synthesis has been assimilated into industry (up to a scale 7−40 kg h^{-1} of magnesium) for production of oligoethylsiloxanes with low (5−20%) and high content (up to a 40%) of the terminal triethylsiloxy groups.

The research described above was based on our original concept of R/D of the Grignard synthesis. The conclusions given below are part of this concept.

(1) It is necessary to use the minimal concentration of catalyst for the formation of Grignard reagent. This is a basic and novel principle of the chemistry and technology of partially solvated Grignard reagents.

(2) There must be a certain agreement between the rate of formation of Grignard reagent and the rate of formation of products from Grignard reagent. This is a basic and novel principle of the chemistry and technology of a mixture organoethoxy- and organochlorosilanes.

(3) It is necessary to use the minimal steady-state concentration of Grignard reagent. This is a basic and novel principle of the chemistry and technology of Grignard reagents (the use of the minimal steady-state concentration of the product of the limiting stage as a method for understanding and for R/D of chemical processes).

(4) It is necessary to use (a) the excess of the granulated magnesium as grinding balls and (b) the columnar apparatus with the stirrer as a mill and (c) the counterflow of the magnesium and the reagent mixture. This is a basic principle of the chemistry and technology of continuous organomagnesium syntheses.

We intend to outline these concepts in our further publications.

Experimental Section

General Procedures. All reagents and solvents were obtained from SILANE and used without further purification. The purity of starting magnesium L-29 and MG-90 were 96−98% and 96−98%, respectively.

The liquid phase obtained in the synthesis was separated by centrifugation and analyzed on an LKhM-80 chromatograph[5] (2 m × 4 mm column, 5% E-301 on Celite 545, detector temperature 350 °C, vaporizer temperature 350 °C, programmed heating from 50 to 300 °C at a rate of 12 deg min^{-1}, carrier gas helium, flow rate 50 mL min^{-1}, detector current 100 mA).

The content of magnesium in the product was determined from the amount of hydrogen released after the decomposition of the sample (0.3−0.5 g) with 20 mL of sulfuric acid (1:3), using a 2 m × 4 mm column packed with zeolite 5A (0.250−0.315 mm grains) and the calibration curve. Temperatures of the vaporizer, the column, and the detector were 50, 35 and 40 °C, respectively. The carrier gas (argon) flow rate was 60 mL min^{-1}. The detector current was 100 mA.

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[46] Klokov, B. A.; Kulinskii, A. I.; Kuz'min, D. S.; Anochin, N. Ph.; Min'kova, N. I. *All-Russia conference "Organosilicon compounds: Synthesis, characteristics, use"* Moscow, **2000**, C 108.

Table 6. **Parameters of continuous organomagnesium synthesis of ethyl-substituted silanes**

entry	supply rate of **1** (g h^{-1})	feed rate of the reaction mixture (mL h^{-1})	temperature in indicated zones of synthesis reactor (Figure 1a,1c) (°C)					heat removal from the first reaction zone (kcal h^{-1})
			first	second	third	fourth	separator	
5[a]	75−85	1050−1150	84−94	67−96	69−83	44−57	36−57	196−228
6[a]	105−110	1360−1440	91−96	74−77	64−70	88	74−77	284−300
7[b]	50	720−760	84−91	74−84	74−81	75−79	75−79	*c*

entry	feed rate[d] of the reaction mixture (mL h^{-1})	temperature in indicated zones of synthesis reactor (Figure 1b) (°C)									
		first	second	third	fourth	fifth	sixth	seventh	eighth	ninth	10th
3	1210−1310	65−71	77−81	72−78	75−85	84−85	78−81	71−75	63−67	53−58	57−62
4a	1290−1310	62−65	74−76	78−82	79−81	70−73	71−77	65−72	59−66	50−56	54−60
4b	1280−1360	62−65	74−76	78−82	79−81	70−73	71−77	65−72	59−66	50−56	54−60

[a] Reactor (Figure 1a). [b] Reactor (Figure 1c). [c] Not determined. [d] The supply rate of magnesium is 100 g h^{-1}.

The hydrogen content was determined from the peak height on the 8-mV scale of potentiometer from two parallel findings.

The ethylmagnesium chloride content was determined from the amount of ethane formed after the sample (3.0−9.0 g) was decomposed with distilled water (20 mL) using a 2 m × 4 mm column packed with Polysorb-1 and the calibration curve. Temperatures of the vaporizer, the column, and the detector were 50, 35, and 40 °C, respectively. The carrier gas (helium) flow rate was 60 mL min^{-1}. The detector current was 100 mA. The ethane content was determined from the peak area from two parallel findings.

The gaseous phase from the reactor separator was analyzed on an LKhM-8MD chromatograph (2 m × 3 mm column packed with Polysorb-1). The detector and vaporizer temperature was 200 °C; the columns were heated in programmed mode with a 12 deg min^{-1} heating rate over the temperature range from 35 to 200 °C. The carrier gas (helium) flow rate was 30 mL min^{-1}. The detector current was 90 mA.

The continuous synthesis was carried out using a column apparatus (Figure 1) divided along the vertical into four or 10 zones by jackets. The zones are numbered from the bottom to the top. The continuous processes were performed according to the procedure given previously.[47]

The parameters of continuous syntheses are listed in Table 6.

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(47) Klokov, B. A. *Org. Process Res. Dev.* **2000**, *4*, 122.