Organic Process Research & Development **2000**, *4*, 49–54

Continuous and Batch Organomagnesium Synthesis of Ethyl-Substituted Silanes from Ethylchloride, Tetraethoxysilane, and Organotrichlorosilane for Production of Polyethylsiloxane Liquids. 1. Batch One-Step Synthesis of Ethylethoxysilanes and Ethylchlorosilanes

Boris A. Klokov*

Silane Joint-Stock Company, 14 Zaitsev street, Dankov, Lipetsk Region, 399820 Russia

Abstract:

Development of batch one-step manufacturing process for ethylethoxy- and ethylchlorosilanes is desribed. The methodology of synthesis of ethyl-substituted silanes has been improved. The important factors for the successful synthesis have been determined. Among them are the replacement of the part tetraethoxysilane 3 by ethyltrichlorosilane 10, the optimum concentration of 3 and 10 resulting in high yield of triethylsilanes, low duration of synthesis, and high selectivity of Grignard reagent. Batch one-step synthesis has been assimilated into industry (up to a scale 240 kg of magnesium) for production of oligoethylsiloxanes with the high content (>40%) of a terminal triethylsiloxy group. The rules for R/D process of the Grignard synthesis are described.

Introduction

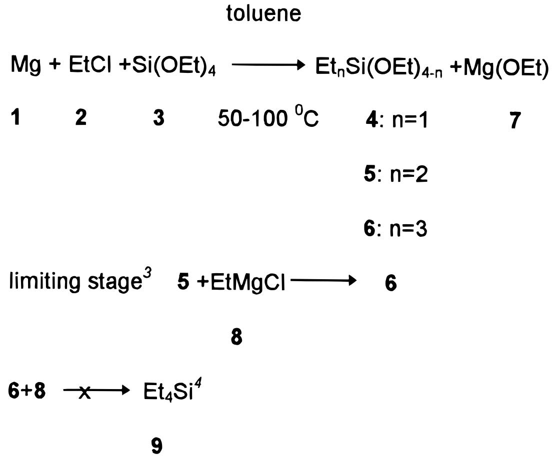
Batch one-step organomagnesium synthesis of ethylethoxysilanes is widely used in industry for production of valuable polyethylsiloxane liquids[1] and for production of silicone intermediates (polyolefin catalysis)[2] (Scheme 1).

In this process tetraethoxysilane **3** performs two functions—it is a catalyst for the formation of ethylmagnesium chloride **8** and a reagent in the subsequent formation of ethylethoxysilanes **4**−**6**.[3−8]

The advantages of this process lie in the freedom from flammable solvents (ethers) and the lack of tetraethylsilane **9**.

However, this process usually has severe disadvantages when applied to the industrial continuous synthesis.[3,9−11]

Scheme 1



These severe disadvantages are conditioned by the low rate of the limiting stage (Scheme 1), resulting in low conversion of Grignard reagent **8**, low content of ethylsilane **6**, and high viscosity of the product, resulting in plugging of the outlet of the reactor separator. Another disadvantage of this process is using of expensive ethoxysilane **3**.

To develop a more inexpensive and practical synthesis of ethyl-substituted silanes we investigated the new synthetic method illustrated in Scheme 2.

In this method the commercially available and inexpensive ethyltrichlorosilane **10** serves as the starting material instead of ethoxysilane **3**.

Results and Discussion

The effect of different parameters on composition of **4**−**6** and **9**−**12** and conversion of **8** was studied and is discussed in the following sections. We also summarise the results reported previously[3,12,13] and the recent data.

---

(1) Khananashvili, L. M.; Andrianov, K. A. *Technology of Organoelement Monomers and Polymers* [in Russian]; Khimiya: Moscow, 1983.

(2) Arcles, B. In *Handbook of Grignard Reagents*; G. S. Silverman, P. E. Rakita, Ed.; Dekker: New York, 1996; Chapter 32.

(3) Klokov, B. A. *Metalloorg. Khim.* **1992**, *5(1)*, 83 *(Organomet. Chem. in the USSR* **1992**, *5(1)*, 43).

(4) DiGiorgio, B. P. A.; Strong, W. A., Sommer, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 1380.

(5) Andrianov, K. A. Patent No. RU 53544, 1937; *Byull. Izobret.* **1938**.

(6) Andrianov, K. A.; Gribanova, O. I. *Zh. Ob. Khim.* **1938**, *8(6)*, *552 (Russ. J. Gen. Chem.* **1938**, *8(6)* (Engl. Transl.).

(7) Andrianov, K. A.; Gribanova, O. I. *Zh. Ob. Khim.* **1938**, *8(6)*, 558 *(Russ. J. Gen. Chem.* **1938**, *8(6)* (Engl. Transl.).

(8) Andrianov, K. A. *Methods of Organometallic Chemistry: Silicon* [in Russian]; Nauka: Moskow, 1968.

(9) Vavilov, V. V.; Velikii, V. V.; Gerlivanov, V. G.; Kalliopin, L. E.; Klokov, B. A.; Medvedev, A. D.; Sakhiev, A. S.; Ufimtsev, N. G. Patent No. RU 726825, 1977; *Byull. Izobret.* **1985**, *30*.

(10) Kalliopin, L. E.; Simanenko, Z. A.; Sakhiev, A. S.; 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]; filed at ONIITEKhIM, Cherkassy, February 6, 1984, No 127-khp-D-84.

(11) Klokov, B. A.; Ufimtsev, N. G.; Grishutin, Yu. P.; Simanenko, Z. A.; Sakhiev, A. S.; Kalliopin, L. E.; Sobolevskii, M. V.; Vavilov, V. V.; Gerlivanov, V. G. Abstracts of Papers, *Magnesium Alloys for Modern Technics* [in Russian]; All-Union Meet., Moscow, Dec. 6−8, 1988, Moscow: Nauka, 1992; p 185.

(12) Klokov, B. A. *Continuous Controlled Organomagnesium Synthesis of Ethylethoxy(chloro)silanes for Oligoethylsiloxanes*. Dissertation. Moscow, 1984.

10.1021/op990049t CCC: $19.00 © 2000 American Chemical Society and The Royal Society of Chemistry
Published on Web 12/02/1999

Scheme 2

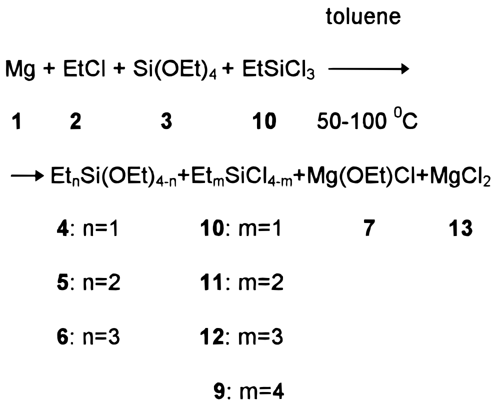


Table 1. **Effect of concentration of 3 and 10 on the composition ethylsilanes and the conversion (*C*) of 8 in a batch one-step process**[a]

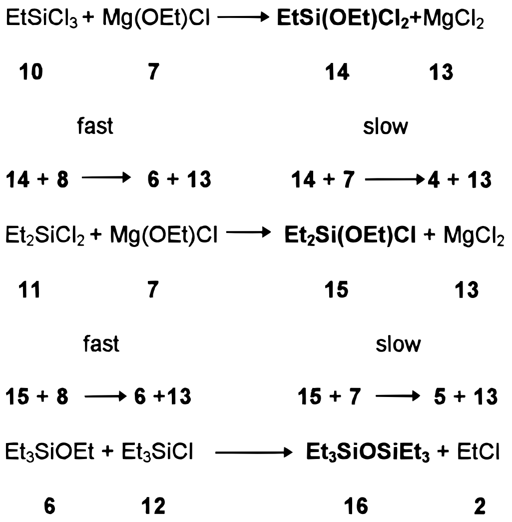
	M		yield (%) for compounds listed in Scheme 2								*C* of **8**
entry	**3**	**10**	**3**	**4**	**5**	**6**	**10**	**11**	**12**	**16**	(%)
1[b]	1.200	0.000	0.0	0.0	94.0	6.0	0.0	0.0	0.0	0.0	82.7
2	1.172	0.232	0.0	9.2	68.2	16.6	0.0	3.2	0.0	2.8	92.1
3	1.040	0.464	7.7	15.1	46.3	21.7	0.0	7.5	0.0	1.7	84.5
4	0.910	0.696	7.0	12.9	35.4	25.9	3.0	14.1	0.0	1.7	85.9
5	0.786	0.928	3.3	4.7	33.7	27.3	4.5	24.7	0.0	1.8	92.8
6	0.650	1.160	0.9	2.7	23.6	26.8	12.6	29.4	2.0	2.0	90.2
7	0.522	1.392	4.3	4.1	13.2	17.2	34.2	22.9	2.7	1.4	68.4

[a] [EtCl] = 3.000 M; duration − 1 h; temperature 60 °C; molar ratio: **1**/**2** = 1.0; **2**/**3** = 2.3; **2**/**10** = 1.3. [b] For comparison.

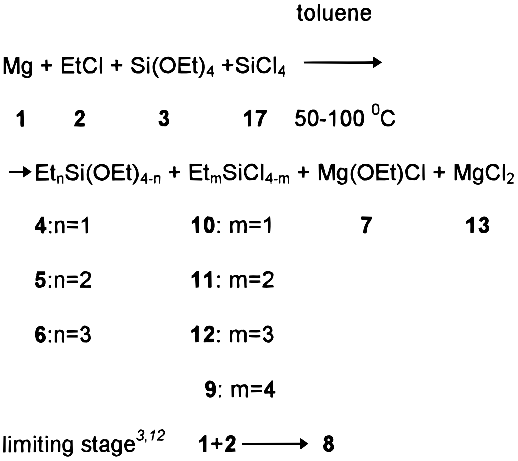
Effect of Concentration of 3 and 10. The experimental results (Table 1) show that the yield of triethylethoxysilane **6** and the conversion of ethylmagnesium chloride **8** are greater when the initial mixture contains ethylsilane **10** (entries 2−6). These results also show that the relative content of ethylchlorosilanes are much lower than relative content of ethyltrichlorosilane in its mixture with tetraethoxysilane. In addition, there is hexaethyldisiloxane **16** in the products.

An increase in triethylsilane **6** in the product (Table 1) and low yields of chlorosilanes are explained by reactions (Scheme 3). Note that reactivity of silanes increases in the order ethoxysilanes < chlorosilanes < ethoxychlorosilanes.

Scheme 3. **Side processes of synthesis of ethyl-substituted silanes**[12,14−16]



Scheme 4



Scheme 3 was confirmed experimentally.[12,14−16] By taking into account published results,[15,16] a series of reactivity of chloro-substituted silanes with respect to ethoxymagnesium chloride under the conditions of batch organomagnesium synthesis is as follows: **10** > **11** ≫ **12**.

These side processes (Scheme 3) block tetraethylsilane **9** formation from **12**.

The relative contents of the reactions products (Table 1) show that the rates of chlorosilanes (**10**,**11**) ethoxylation, and their subsequent conversion to silane **6** are higher than the rate of ethoxysilane **5** alkylation by **8**.

These results are similar to those obtained in synthesis of the monomers **4**−**6**, **9**−**12** from the mixture of **3** and tetrachlorosilane **17** (Scheme 4).[3,12]

Since silane **10** is an intermediate product in this process (Scheme 4), there is no question that the reaction of Grignard reagent **8** formation is also the limiting stage of the synthesis (Scheme 2). The rate of the limiting stage (Scheme 4) was found to be directly proportional to catalyst **3** loading (concentration).

Since the kinetics of formation of organomagnesium halides had been well studied, the analysis of the synthesis of ethylethoxy(chloro)silanes was considerably eased.

The effect of concentration of **3** (and **10**) on conversion of **8** and yields of silanes **4**−**6**, **9**−**12** is discussed more closely below.

---

(13) Klokov, B. A. Abstracts of Papers, *First Regional Conference on Organic Chemistry* [in Russian]; Lipetsk, Nov. 26−28, 1997, Lipetsk, 1997, p 52.

(14) Klokov, B. A.; Sobolevskii, M. V.; Sakhiev, A. S.; Bezlepkina, V. M. *Organomagnesium Synthesis of Ethyl-Substituted Organosilicon Monomers. III. Certain Side Reactions in Ethylchlorosilane Synthesis (in the presence of diethyl ether)* [in Russian]; filed at ONIITEKhIM, Cherkassy, April 12, 1982, No. 407-khp-D-82.

(15) Klokov, B. A.; Sobolevskii, M. V.; Sakhiev, A. S.; Simanenko, Z. A.; Bezlepkina, V. M.; Yakovleva, L. N. *Organomagnesium Synthesis of Ethyl-Substituted Organosilicon Monomers. VI. Certain Side Reactions in Organomagnesium Synthesis of Mixtures of Ethylethoxysilanes and Ethylchlorosilanes* [in Russian]; Filed at ONIITEKhIM, Cherkassy, February 1, 1984, No. 128-khp-D-84.

(16) Klokov, B. A. *Zh. Prikl. Khim.* **1998**, *71(10)*, 1752 (*Russ. Jorn. Appl. Chem.* **1998**, *71(10)*).

Scheme 5. **Processes lovering reactivity of ethylmagnesium chloride 8**

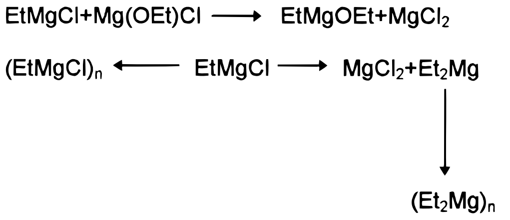


Table 2. **Effect of concentration of 3 and 17 on the composition of ethylsilanes and the conversion (*C*) of 8 in a batch one-step process**[a]

	M		yield (%) for compounds listed in Scheme 4								*C* of **8**
entry	**3**	**17**	**3**	**4**	**5**	**6**	**10**	**11**	**12**	**16**	(%)
1[b]	1.363	0.000	3.3	22.2	71.9	2.6	0.0	0.0	0.0	0.0	80.4
2	1.227	0.136	6.2	18.8	66.0	9.0	0.0	0.0	0.0	0.0	82.5
3	1.090	0.273	4.5	15.7	61.4	18.4	0.0	0.0	0.0	0.0	90.1
4	0.954	0.409	12.5	18.9	43.5	25.1	0.0	0.0	0.0	0.0	86.0
5	0.818	0.545	10.8	12.3	33.6	21.9	5.6	15.3	0.0	0.5	86.4
6	0.682	0.681	4.5	5.1	27.3	27.3	10.8	23.7	1.3	0.0	94.0
7	0.545	0.818	15.9	4.2	14.6	7.6	28.5	21.6	7.6	0.0	71.6

[a] [EtCl] = 3.000 M; duration − 1 h; temperature 60 °C; molar ratio: **1**/**2** = 1.0; **2**/**3** = **2**/**17** = 2.2. [b] For comparison.

The conversion of **8** was less than 70% (entry 7) because of the low quantity of catalyst **3** (**3**:**2** = 0.17).

The fact that the reaction products contain practically no **3** or **4** (entries 6 and 7) indicates relative high rates of ethoxysilanes **4** and **5** formation; a high chlorosilane **10** contents suggests a rather low rate of chlorosilane **11** formation. Therefore, the reactivity of ethoxysilanes **3** and **4** (catalysts of ethylmagnesium chloride **8** formation) toward **8** is higher than that of chlorosilane **10** for the minimum quantity of catalyst (less than 0.786 M). It is likely that this effect stems from formation of complexes **8** with **3** and **4**.[17]

The conversion of **8** and yield of silane **6** are greatest (92.8 and 27.3%, accordingly; entry 5) for the minimum (optimum) quantity of catalyst (0.786 M; **3**:**2** = 0.26). This effect stems from the greatest reactivity of **8** determined by a low degree of a solvation of **8** by solvating species, e.g., ethoxysilanes and ethoxymagnesium chloride **7**.

The fact that the reaction products contain of **3** and conversion of **8** less than 90% (entries 3 and 4) indicates relative less reactivity of part of **8**. It is possible that the rate of **8** formation is higher than rates of ethylsilanes **4**−**6**, **9**−**12** formation (entries 3 and 4). It that case part of ethylmagnesium chloride **8** will form ethyl(ethoxy)magnesium, solvating species (the degree of the solvation of **8** at least by one-two molecules per atom of magnesium), and oligomers which lower the reactivity of **8** (Scheme 5).[18−23]

Scheme 6

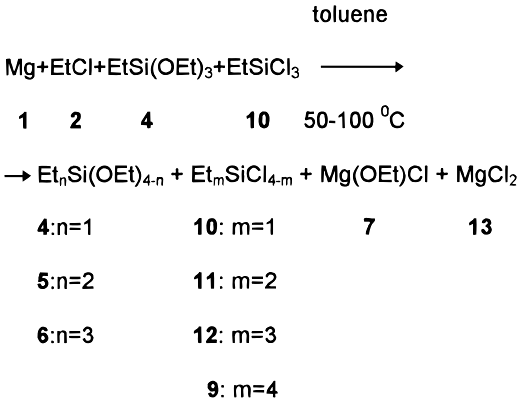


Table 3. **Effect of molar ratio 4 to 10 on the composition of ethylsilanes and the conversion (*C*) of 8 in a batch one-step process**[a]

	molar ratio	yield (%) for compounds listed in Scheme 6							*C* of **8**
entry	**4**:**10**	**4**	**5**	**6**	**10**	**11**	**12**	**16**	(%)
1	9:1	1.3	86.4	10.0	0.0	2.3	0.0	0.0	84.5
2	8:2	0.0	74.2	17.0	1.2	5.2	1.1	1.3	92.2
3	7:3	1.4	62.1	18.5	2.2	14.3	1.5	0.0	90.2
4	6:4	4.6	56.3	18.0	1.8	17.1	2.2	0.0	89.0
5	5:5	1.2	43.4	18.0	0.0	29.7	5.2	2.5	97.3
6	4.5:5.5	3.6	33.5	19.3	4.0	29.0	8.3	2.3	95.9

[a] [EtCl] = 3.000 M; duration − 1 h; temperature 60 °C; mole ratio: **2**/**4** = **2**/**10** = 1.3; [**4** + **10**] = 2.308M.

Table 4. **Effect of temperature (*T*) on the composition of ethylsilanes and the conversion (*C*) of 8 in a batch one-step process**[a]

	T	yield (%) for compounds listed in Scheme 2								*C* of **8**
entry	(°C)	**3**	**4**	**5**	**6**	**10**	**11**	**12**	**16**	(%)
1	50	4.3	5.5	30.0	24.1	6.3	23.5	5.2	1.1	91.3
2	70	5.8	5.1	30.5	17.4	6.1	21.9	11.7	1.5	90.8
3	80	1.6	5.1	39.9	19.8	8.6	24.0	0.0	1.0	86.7
4	90	11.0	7.3	29.7	12.3	12.8	16.5	8.0	2.4	76.5

[a] [EtCl] = 3.000 M; duration − 1 h; temperature 60 °C; concentration: **3** = 0.786 M and **10** = 0.928 M.

The fact that the conversion of **8** is again higher than 92% (entry 2) indicates a relative higher rate of the process (Scheme 2), which is due to the higer quantity of **15** (Scheme 3).

The optimum concentration **3** and **10** for the reaction are about 0.786 and 0.928 M, respectively (entry 5).

These results are similar to those obtained in synthesis of the monomers **4**−**6**, **9**−**12** from the mixture of **3** and tetrachlorosilane **17** (Scheme 5; Table 2).[12] In this case ideal concentration of **3** and **17** for the reaction are about 0.682 and 0.681 M, respectively (entry 6; molar ratio **3**:**2** = 0.23). This means that there are certain ideal concentrations **4** and **10** (Scheme 6).

Effect of Concentration of 4 and 10. The experimental results (Table 3) support this assumption. In this case the

---

(17) Voronkov, M. G.; Mileshkevich, V. P.; Yuzhelevskii, Yu. A. *The Siloxane Bond* [in Russian]; Nauka: Novosibirsk, 1976.
(18) Bryce-Smith, D.; Cox, G. F. *J. Chem. Soc.* **1961**, 1175.
(19) Bryce-Smith, D. *Bull. Soc. Chim. Fr.* **1963**, 1418.
(20) Glaze, W. N.; Selman, C. M. *J. Organomet. Chem.* **1966**, *5*, 477.
(21) Wakefield, B. J. *Organomet. Chem. Rev.* **1966**, *1*, 131.
(22) Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.
(23) Bickelhaupt, F. *J. Organomet. Chem.* **1994**, *475*, 1.

Table 5. **Effect of molar ratio 2 to 3 and 10 on the composition ethylsilanes and the conversion (*C*) of 8 in a batch one-step process**[a]

entry	molar ratio **2** to **3** and **10**		yield (%) for compounds listed in Scheme 2									*C* of **8** (%)
			3	**4**	**5**	**6**	**10**	**11**	**12**	**9**	**16**	
1	2.0	1.0	10.6	6.8	20.2	20.0	16.2	22.5	2.6	0.0	1.1	90.0
2	2.2	1.2	7.1	6.8	24.1	22.6	9.3	22.6	6.0	0.0	1.5	91.8
3	2.4	1.4	1.5	4.2	35.8	25.6	3.4	24.4	4.4	0.0	0.7	90.9
4	2.6	1.6	0.0	0.0	42.5	29.8	0.0	27.7	0.0	0.0	0.0	85.9
5	2.8	1.8	0.0	0.0	33.5	36.5	3.0	12.1	12.0	0.8	2.1	86.7
6	3.0	2.0	0.0	0.0	30.4	40.6	3.1	5.8	13.4	1.9	4.8	84.7
7	3.3	2.3	0.0	0.0	26.4	44.7	2.9	4.6	16.5	3.2	1.7	78.5

[a] [EtCl] = 3.000 M; duration − 1 h; temperature 60 °C; mole ratio **3**:**10** = 0.782 (0.726:0.928).

Table 6. **Effect of concentration of 3 and 10 on the composition of ethylsilanes in a batch laboratory (L) or an industrial (I) one-step process**[a]

entry	M		method	yield (%) for compounds listed in Scheme 2								
	3	**4**		**3**	**4**	**5**	**6**	**10**	**11**	**12**	**16**	$\mathbf{X}_{1+2}$[b]
1	1.172	0.232	L	0.0	12.1	66.3	16.6	0.0	2.6	0.0	2.4	0.0
2			I	2.0	8.7	63.6	11.3	0.0	0.0	1.9	10.5	2.0
3			I	4.0	6.6	58.3	17.7	0.0	0.0	1.1	5.9	6.4
4	1.040	0.464	L	7.7	18.1	44.1	20.7	0.8	4.2	0.0	4.4	0.0
5			I	9.1	8.3	50.3	22.8	0.9	1.6	0.9	2.4	3.7
6			I	12.0	11.9	41.2	23.2	0.0	0.0	2.3	5.4	4.0
7	0.786	0.928	L	3.9	6.3	31.7	22.1	4.2	21.5	3.0	4.6	0.0
8			I	7.9	3.9	25.6	29.2	3.1	13.1	2.4	11.0	3.8

[a] [EtCl] = 3.000 M; duration − 1 h; temperature 60 °C; mole ratio: **1**/**2** = 1.0; **2**/**3** = 2.3; **2**/**10** = 1.3. [b] Oligoethylsiloxanes into regenerated toluene.

Table 7. **Effect of molar ratio 2 to 3 and 10 on the composition of ethylsilanes in a batch industrial one-step process**[a]

entry	molar ratio **2** to **3** and **10**		yield (%) for compounds listed in Scheme 2									
			3	**4**	**5**	**6**	**10**	**11**	**12**	**9**	**16**	$\mathbf{X}_{1+2}$[c]
1	2.3	1.3	7.9	3.9	25.6	29.2	3.1	13.1	2.4	0.0	11.0	3.8
2	2.4	1.4	2.4	2.7	30.9	33.2	1.3	6.3	5.3	0.5	10.8	5.0
3	2.6	1.6	0.0	1.8	40.0	36.6	1.6	8.9	8.3	0.0	2.8	0.0
4[b]	2.6	0.0	0.0	0.0	73.1	16.4	0.0	0.0	0.0	0.0	8.2	2.3

[a] Molar ratio **3**:**10** = 0.782 = (0.726:0.928). [b] For comparison. [c] Oligoethylsiloxanes into regenerated toluene.

ideal concentrations of **4** and **10** for the reaction are about 1.154 and 1.154 M, respectively (entry 5).

Effect of Temperature. The reactions were carried out in the temperature range 50−90 °C, and it was observed that the better temperatures for the reaction were 50−70 °C; at temperatures above 80 °C the conversion of **8** was less than 80% (Table 4). This is probably due to a decreased ethyl chloride **2** solubility at temperatures higher than 70 °C (**2** is soluble in mixture **2**, **3**, **10**, and toluene but is boiled out at above 70 °C).

In principle, the temperature has little if any effect on the composition ethylsilanes **4**−**6**, **9**−**12**. The duration of synthesis has also little effect on the composition of ethylsilanes.

These results also support the conclusion that the limiting stage of process (Scheme 2) is **1** + **2** → **8**. (The rate of this reaction is little affected by temperature).

Effect of Molar Ratio of 2 to 3 and 10. Reactions were carried out in the molar ratio range 2.0−3.3 (for **3**) and 1.0−2.3 (for **10**), and it was observed that the composition of the ethyl-substituted silanes can be regulated by changing the molar ratio of the starting materials (Table 5).

Conversion of **8** was found to decrease from 90−92% to 79−85% with a decrease in molar ratio **3**:**2** from near 0.25 (entries 1,2) to near 0.17 (entries 6,7).

At molar ratio **2**:**3** = 2.6−3.3 were obtained the better compositions of **4**−**6**, **9**−**12** (the lack of **3** and high yield (30−63%) triethyl-substituted silanes **6** + **12** + **16**) at low duration of synthesis (1 h at 60 °C)/entries 4−7, Table 5/. By comparison, two other syntheses (ethylethoxy- or ethylchlorosilanes) give either a 60−70% yield triethylsilane **6** but at much higher duration (12 h by at 100−130 °C) (synthesis of ethylethoxysilanes)[4,8,24,25] or only a 30−35%

---

(24) DiGiorgio, B. P. A.; Strong, W. A., Sommer, L. H. *J. Am. Chem. Soc.* **1955**, *77*, 6647.

(25) Andrianov, K. A.; Levshuk, M. Ja.; Golubtsov, S. A.; Krasovckaja, M. A. Patent No. RU 127259, 1948; *Byull. Izobret.* **1960**, *7*.

Table 8. **Effect of duration (*D*) of synthesis at 60 and 100 °C on the composition of ethylsilanes in a batch industrial one-step process**[a]

	D (h)		yield (%) for compounds listed in Scheme 2									
entry	60 °C	100 °C	**3**	**4**	**5**	**6**	**10**	**11**	**12**	**9**	**16**	$\mathbf{X}_{1-3}$[b]
1	1	0	0.0	1.3	23.8	32.6	1.4	4.9	5.3	0.9	17.1	11.4
	1	3	0.0	1.3	23.9	31.8	1.4	5.2	5.1	0.9	17.1	14.7
2	1	0	2.7	1.8	26.9	32.7	4.0	12.7	4.6	0.0	7.5	5.1
	1	3	2.4	2.5	31.5	29.6	2.5	8.2	6.9	0.0	10.4	4.6
3	1	0	1.3	2.3	27.0	35.6	1.7	5.2	4.9	0.0	1.7	20.3
	1	3	1.4	2.3	24.7	28.1	1.5	3.1	3.2	0.0	18.3	17.4
4	1	0	0.7	1.9	37.4	36.4	2.2	10.1	8.3	0.0	2.4	0.0
	1	3	0.0	1.8	40.0	36.6	1.6	8.9	8.3	0.0	2.8	0.0

[a] [EtCl] = 3.000 M; molar ratio: **1**/**2** = 1.0; **2**/**3** = 2.6; **2**/**10** = 1.6; **3**: **10** = 0.782 (0.726:0.928). [b] Oligoethylsiloxanes into regenerated toluene.

yield of triethylchlorosilane **12** (synthesis of ethylchlorosilanes).[4,8,12,14,26−32]

These results also support the conclusion that the limiting stage of process (Scheme 2) is **1** + **2** → **8**.

Effects of Different Parameters on Composition of 4−6, 9−12 in Manufacturing Process. The process as described was transferred to the manufacturing process up to a scale of 240 kg of **1**.[33] The effects of different parameters of composition of **4**−**6**, **9**−**12** in manufacturing process (Tables 6−8) are similar to those obtained in syntheses on laboratory (pilot) scale (Tables 1−5). These results show that simultaneous synthesis of ethyl-substituted silanes (chloro- and ethoxy-) can be scaled up to an industrial level.

Batch one-step synthesis (Scheme 2) has been assimilated into industry (in 1981) for production of oligoethylsiloxanes with the higher content (>40%) of a terminal triethylsiloxy groups.

The main results of this work were patented.[33]

Conclusion

We have improved the methodology of the synthesis of ethyl-substituted silanes. Previous routine methods (synthesis of ethylchlorosilanes or of ethylethoxysilanes), which exploited as a 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) the replacement of a some ethoxysilane **3** by clorosilane **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 rate of formation of Grignard reagent and rate of formation of ethylsilanes. The better results were obtained at molar ratio **2**:**3** = 2.6−3.3 (the lack of **3** and high yield (30−63%) triethyl-substituted silanes **6** + **12** + **16**). Batch one-step synthesis has been assimilated into industry (up to a scale 240 kg of **1**)[33] for production of oligoethylsiloxanes with the high content (>40%) of a terminal triethylsiloxy groups.

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

It is necessary to use the minimal concentration of catalyst for the formation of Grignard reagent.

There must be a certain agreement between the rate of formation of Grignard reagent and the rate of formation of products from Grignard reagent.

It is a necessary to use the minimal steady-state concentration of Grignard reagent.

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 liquid phase obtained in the synthesis was separated by centrifugation and analyzed on an LKhM-80 chromatograph[26] (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 12° min^{-1}, carrier gas helium, flow rate 50 mL min^{-1}, detector current 100 mA).

Batch One-Step Synthesis of Ethyl-Substituted Silanes. Magnesium turnings (73 g, 3.0 mol) were charged into a 2-L round-bottom four-necked flask equipped with a mechnical stirrer with a hydroseal, a reflux condenser, a thermometer and a dropping funnel. Magnesium was heated to 70−75 °C and stirred at this temperature for 20 min. To the Mg turnings was quickly added a portion (20−40 mL) of a mixture of **2** (210 mL, 3.000 mol), **3** or **4** and **10** or **17**, and toluene (of a given composition). The reaction self-initiated within 10−15 min. The remaining solution of the mixture was added (continuous addition) into the flask over 40−50 min at the prescribed synthesis temperature mode (50−90 °C); a cooling bath was needed to keep the temperature within this range. When the addition was complete, the

---

(26) Klokov, B. A. *Zh. Prikl. Khim.* **1995**, *68(1)*, 114 (*Russ. Jorn. Appl. Chem.* **1995**, *68(1)*, 100).

(27) Bugden, A. *Ber.* **1911**, *44*, 2640.

(28) Bugden, A. *Ber.* **1912**, *45*, 707.

(29) Alfrey, T.; Honn, F. I.; Mark, H. I. *J. Polym. Sci.* **1946**, *1(2)*, 102.

(30) Man, F. D.; Steenis, J. V.; Waterman, H. I. *Recl. Trav. Chim. Pays-Bas.* **1948**, *67(11)*, 864.

(31) Rust, J. B.; McKenzie, C. A. U.S. Patent 2,426,121, 1944, *Chem. Abstr.*, **1948**, *42*, 921.

(32) Rust, J. B.; McKenzie, C. A. U.S. Patent 2,426,122, 1944, *Chem. Abstr.*, **1948**, *42*, 921.

(33) Klokov, B. A.; Ufimtsev, N. G.; Novikov, V. I.; Balukov, Ju. L.; Eremina, A. A.; Grinevich, K. P.; Truchin, A. Ph. Patent No. RU 1203867, 1983; *Byull. Izobret.* **1994**, *17*, 176.

mixture was stirred for 1 h at 60 °C, and a sample was withdrawn to analyse the reaction products. Results of these syntheses are given in Tables 1−5.

Acknowledgment

The author is grateful to the collaborators in GNIIKhTEOS (State Research Institute of Chemical Technology of Organoelement Compounds), and SILANE, which are the authors of the patent,[33] for helpful discussion aimed at improving the properties of the final products and to all those in SILANE Process R/D and Chemical Manufacturing who have worked on polyethylsiloxane liquids in the past 18 years.

Received for review May 26, 1999.

OP990049T