

SYNTHESIS OF TRIORGANYLCHLOROSILANES BY
 CATALYTIC REACTION OF TRIORGANYLSILANES
 WITH CHLOROBENZENE

Yu. I. Khudobin, N. A. Andreeva,
 N. P. Kharitonov, and M. G. Voronkov

UDC 542.97:547.1'128

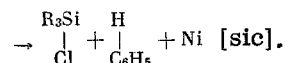
Previously [1, 2] we had shown that triorganylsilanes react with halohydrocarbons in the presence of colloidal nickel by the following scheme.



In the present communication we report the results of studying the effect of the structure of the organic substituents on the silicon atom in triorganylsilanes and the amount of catalyst on the reactivity of the Si-H bond in R_3SiH . The experimental data on the reaction of triorganylsilanes with chlorobenzene are given in Table 1.

The hydrogen atom, attached to silicon, is not replaced by chlorine when the triorganylsilanes are reacted with chlorobenzene in the absence of a catalyst under the studied conditions. The reaction rate increases noticeably with increase in the amount of colloidal nickel (Fig. 1), but here the yield of the formed triorganylchlorosilane shows little change, and always remains high (96-99%). The structure of the triorganylsilanes has an important effect on the reaction rate. The rate of the process decreases with increase in the electronegativity of the substituents on the silicon atom. Substituents that have a branched structure or a longer hydrocarbon chain also decrease the reaction rate due to the steric effect (see Table 1).

In all probability, the reaction of triorganylsilanes with chlorobenzene on a nickel catalyst is one of bimolecular nucleophilic substitution (S_N2 type according to Ingold-Hughes), the mechanism of which can be depicted by the following scheme:



*The colloidal nickel was obtained by the reduction of anhydrous nickel chloride with the appropriate triorganylsilane [3, 4].

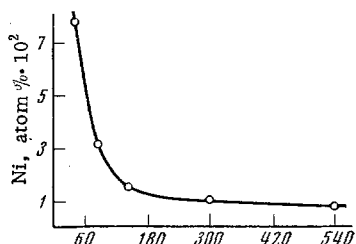


Fig. 1. Relation between reaction rate of ethyl-di-n-butylsilane with chlorobenzene (mole ratio 1:1) at 150-134°C and the amount of colloidal nickel (g-atom of Ni/mole of silane × 100).

I. V. Grebenshchikov Institute of Silicate Chemistry, Academy of Sciences of the USSR, Leningrad. Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 4, pp. 856-859, April, 1974. Original article submitted October 23, 1973.

© 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. Preparation of R₃SiCl by Reaction of R₃SiH with Chlorobenzene; Mole Ratio of R₃SiH: C₆H₅Cl = 1: 1 (0.1 mole of each), Amount of Colloidal Nickel 0.09 g (1.55 atom %)

R ₃ SiCl	Temp. of reaction mixture, °C	Reaction time, min	Yield, %	R ₃ SiCl	Temp. of reaction mixture, °C	Reaction time, min	Yield, %
CH ₃ (C ₂ H ₅) ₂ SiCl *	94—105	525	94	C ₂ H ₅ (i-C ₈ H ₁₇) ₂ SiCl	157—133	186	96,6
CH ₃ (n-C ₈ H ₁₇) ₂ SiCl *	126—109	87	96,4	C ₂ H ₅ (C ₆ H ₅) ₂ SiCl	166—150	201	96,8
CH ₃ (i-C ₈ H ₁₇) ₂ SiCl †	119—110	122	95,8	C ₂ H ₅ (n-C ₈ H ₁₇) ₂ SiCl	165—143	171	95,4
CH ₃ (n-C ₆ H ₁₃) ₂ SiCl *	141—122	90	97,5	C ₂ H ₅ (n-C ₇ H ₁₅) ₂ SiCl	168—146	190	96
CH ₃ (i-C ₆ H ₁₃) ₂ SiCl	136—116	126	96,3	C ₂ H ₅ (C ₆ H ₅) ₂ SiCl	171—152	216	96,8
CH ₃ (n-C ₈ H ₁₇) ₂ SiCl	143—125	100	96,8	C ₂ H ₅ (n-C ₉ H ₁₉) ₂ SiCl	175—153	245	96,1
CH ₃ (i-C ₈ H ₁₇) ₂ SiCl	142—124	120	97,1	C ₂ H ₅ (n-C ₁₀ H ₂₁) ₂ SiCl	175—148	380	96,5
CH ₃ (C ₆ H ₅) ₂ SiCl *	151—140	138	94,5	(n-C ₈ H ₁₇) ₂ SiCl *	143—133	151	96,9
CH ₃ (n-C ₇ H ₁₅) ₂ SiCl	156—141	139	98,5	(n-C ₄ H ₉) ₂ SiCl *	151—133	180	94,5
CH ₃ (n-C ₈ H ₁₇) ₂ SiCl	169—142	161	98,3	(n-C ₆ H ₁₃) ₂ SiCl *	158—128	201	96
CH ₃ (n-C ₉ H ₁₉) ₂ SiCl	169—138	182	97,3	(i-C ₈ H ₁₇) ₂ SiCl *	161—142	224	95,8
CH ₃ (n-C ₁₀ H ₂₁) ₂ SiCl	169—142	246	96,9	(C ₆ H ₅) ₂ SiCl *	172—154	248	94,7
(C ₆ H ₅) ₂ SiCl *	116—110	135	97	(n-C ₆ H ₁₃) ₂ SiCl *	168—134	220	97,1
C ₂ H ₅ (n-C ₈ H ₁₇) ₂ SiCl	136—121	121	92,7	(n-C ₇ H ₁₅) ₂ SiCl *	162—134	231	98,3
C ₂ H ₅ (i-C ₈ H ₁₇) ₂ SiCl	136—117	153	95,5	(n-C ₈ H ₁₇) ₂ SiCl *	161—133	242	97,9
C ₂ H ₅ (i-C ₇ H ₁₅) ₂ SiCl	146—128	160	92,3	(n-C ₉ H ₁₉) ₂ SiCl	172—143	263	98,2
C ₂ H ₅ (n-C ₄ H ₉) ₂ SiCl	150—134	143	97,6	(n-C ₁₀ H ₂₁) ₂ SiCl *	175—155	402	95,7
C ₂ H ₅ (n-C ₅ H ₁₁) ₂ SiCl	160—142	165	96,5				

* New compounds [5].

Simultaneous nucleophilic attack of the chlorine atom on silicon and electrophilic attack of the phenyl carbocation on the hydrogen atom occurs here in the R₃SiH molecule, chemisorbed on the surface of the nickel, with the formation of a four-center intermediate complex that contains pentavalent silicon. It should be mentioned that the reaction rate of triorganylsilanes with chlorobenzene depends on both the inductive and the steric effects of the substituents on the silicon atom (i. e., polarization of the Si—H bond) and on the amount of nickel.

Due to the absence of by-products and simplicity of accomplishment, the catalytic reaction of triorganylsilanes with chlorobenzene studied by us makes it possible to obtain quite pure triorganylchlorosilanes in up to 99% yield. This enabled us to synthesize 35 triorganylsilanes. The physical constants and analysis data of the newly synthesized compounds are given in Table 2; the constants of the previously known compounds coincide with the literature data [5].

EXPERIMENTAL

The starting triorganylsilanes were obtained by the reaction of the methyl- and ethyldichlorosilanes

TABLE 2. Physical Constants and Analysis Data of New Triorganylchlorosilanes

R ₃ SiCl	Bp, °C (P, mm of Hg)	d ₄ ²⁰	n _D ²⁰	MR		Found, %		Calculated, %	
				found	calculated	Si	Cl	Si	Cl
CH ₃ (i-C ₈ H ₁₇) ₂ SiCl	155—155,5	0,8997	1,4390	48,16	48,35	17,20	21,43	17,05	21,52
CH ₃ (i-C ₄ H ₉) ₂ SiCl	186	0,8762	1,4378	57,74	57,64	14,56	18,40	14,57	18,39
CH ₃ (n-C ₈ H ₁₇) ₂ SiCl	231	0,8723	1,4430	67,12	66,94	12,80	16,03	12,72	16,05
CH ₃ (i-C ₆ H ₁₃) ₂ SiCl	220	0,8688	1,4425	67,34	66,94	12,70	15,94	12,72	16,05
CH ₃ (n-C ₇ H ₁₅) ₂ SiCl	127(1,5)	0,8668	1,4491	85,70	85,53	10,21	12,74	10,14	12,80
CH ₃ (n-C ₈ H ₁₇) ₂ SiCl	150(1,5)	0,8621	1,4510	95,28	94,83	9,20	11,51	9,21	11,62
CH ₃ (n-C ₉ H ₁₉) ₂ SiCl	175,5(2)	0,8649	1,4540	104,29	104,12	8,50	10,62	8,43	10,65
CH ₃ (n-C ₁₀ H ₂₁) ₂ SiCl	190(1,5)	0,8645	1,4552	113,40	113,42	7,80	9,82	7,78	9,82
C ₂ H ₅ (n-C ₈ H ₁₇) ₂ SiCl	181	0,8895	1,4392	52,78	52,99	15,68	19,83	15,71	19,83
C ₂ H ₅ (i-C ₈ H ₁₇) ₂ SiCl	179	0,9084	1,4480	52,69	52,99	15,70	19,84	15,71	19,83
C ₂ H ₅ (n-C ₄ H ₉) ₂ SiCl	216,5	0,8832	1,4448	62,32	62,29	13,64	17,14	13,58	17,14
C ₂ H ₅ (i-C ₄ H ₉) ₂ SiCl	205	0,8879	1,4450	62,04	62,29	13,62	17,21	13,58	17,14
C ₂ H ₅ (n-C ₆ H ₁₃) ₂ SiCl	101,5(2,5)	0,8787	1,4475	71,49	71,59	12,10	15,11	11,96	15,09
C ₂ H ₅ (i-C ₆ H ₁₃) ₂ SiCl	237,5	0,8776	1,4470	71,51	71,59	12,20	15,15	11,96	15,09
C ₂ H ₅ (C ₆ H ₅) ₂ SiCl	128(1,5)	1,8873	1,5710	74,59	74,18	11,42	14,31	11,38	14,37
C ₂ H ₅ (n-C ₈ H ₁₇) ₂ SiCl	138(4)	0,8766	1,4512	80,81	80,88	10,66	13,50	10,68	13,48
C ₂ H ₅ (n-C ₇ H ₁₅) ₂ SiCl	180(10)	0,8721	1,4538	90,32	90,18	9,68	12,24	9,65	12,18
C ₂ H ₅ (n-C ₆ H ₁₃) ₂ SiCl	159,5(1,5)	0,8694	1,4545	99,47	99,47	8,76	11,16	8,80	11,11
C ₂ H ₅ (n-C ₉ H ₁₉) ₂ SiCl	177(1)	0,8697	1,4570	108,72	108,77	8,15	10,20	8,09	10,21
C ₂ H ₅ (n-C ₁₀ H ₂₁) ₂ SiCl	211,5(2,5)	0,8686	1,4588	118,04	118,07	7,61	9,43	7,50	9,45
(i-C ₈ H ₁₇) ₂ SiCl	132(4,5)	0,8697	1,4498	85,55	85,53	10,21	12,74	10,14	12,80
(n-C ₈ H ₁₇) ₂ SiCl	239(2,5)	0,8658	1,4612	140,87	141,31	6,34	8,09	6,32	7,98
(n-C ₁₀ H ₂₁) ₂ SiCl	250,5(1,5)	0,8644	1,4615	154,86	155,25	5,76	7,27	5,76	7,28

TABLE 3. Physical Constants, Yields, and Analysis Data of Triorganylsilanes

R ₃ SiH	Yield, %	Bp, °C (P mm of Hg)	d ₄ ²⁰	n _D ²⁰	MR		Mol. wt		Si, %	
					found	calculated	found	calculated	found	calculated
CH ₃ (n-C ₈ H ₁₇) ₂ SiH	72	142(2,5)	0,7932	1,4448	90,71	90,87	269,8	270,58	10,34	10,38
CH ₃ (n-C ₁₀ H ₂₁) ₂ SiH	85	173,5(2,5)	0,8030	1,4498	109,27	109,48	322,5	326,69	8,59	8,60
C ₂ H ₅ (n-C ₈ H ₁₇) ₂ SiH	73	150(1)	0,8009	1,4482	95,17	95,53	283,6	284,61	9,85	9,87
C ₂ H ₅ (n-C ₁₀ H ₂₁) ₂ SiH	86	193(2,5)	0,8074	1,4522	113,90	113,94	340,8	340,71	8,15	8,23
(n-C ₉ H ₁₉) ₃ SiH	74	217(1)	0,8155	1,4564	137,01	137,37	412,3	410,85	7,14	6,84

or trichlorosilane with the appropriate organylmagnesium halides in either absolute diethyl or dibutyl ether. Their physical constants, analysis data, and yields are given in Table 3.

The synthesis of the triorganylchlorosilanes was run in either a pure dry helium or argon atmosphere. The obtained triorganylchlorosilanes were purified by a double distillation over Cu and stored in sealed ampuls, filled with helium or argon, in the absence of light. All of the necessary precautions against the entrance of traces of moisture were taken when determining the physical constants and during analysis. A typical synthesis of a triorganylchlorosilane is given below.

Ethyl-di-n-amylchlorosilane. A mixture of 20.0 g (0.1 mole) of ethyl-di-n-amylsilane, 11.20 g (0.1 mole) of chlorobenzene and 0.09 g of colloidal nickel, obtained by the reduction of 0.20 g (0.16 mole) of anhydrous nickel chloride with ethyl-di-n-amylsilane, was refluxed for 165 min until the temperature of the reaction mixture failed to fall (from 160 to 142°C). Distillation gave 7.72 g (98.8%) of benzene and 22.60 g (96.5%) of ethyl-di-n-amylchlorosilane with bp 240–242°C (736.8 mm) (see Table 2).

CONCLUSIONS

A study was made of the reaction for replacing the hydrogen atom, attached to the silicon in triorganylsilanes, by the chlorine atom when reaction is with chlorobenzene in the presence of colloidal nickel as the catalyst. A probable scheme of the reaction mechanism is given.

LITERATURE CITED

1. Yu. I. Khudobin, B. N. Dolgov, and N. P. Kharitonov, in: Chemistry and Practical Application of Organosilicon Compounds [in Russian], Izd. AN SSSR (1961), No. 6, p. 155.
2. Yu. I. Khudobin, M. G. Voronkov, and N. P. Kharitonov, Izv. Akad. Nauk Latv. SSR, Ser. Khim., 598 (1967).
3. Yu. I. Khudobin, M. G. D'yachenko, N. P. Kharitonov, and P. A. Vasil'eva, Zh. Obshch. Khim., 38, 187 (1968).
4. Yu. I. Khudobin, N. A. Sergeeva, and N. P. Kharitonov, Zh. Obshch. Khim., 38, 412 (1968).
5. V. Bazant, V. Chvalovsky, and J. Rathousky, Organosilicon Compounds, Prague (1965), Vol. 1, Part 1, pp. 132, 180, 237, 353, 506, 521, 558, 608, 665, 684; Vol. 2, Part 2, pp. 50, 80, 81, 125, 126.