Synthesis of (diorgano)chloro(4-chlorobutoxy)silanes

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Some novel (diorgano)chloro(4-chlorobutoxy)silanes were obtained by the reaction of dichlorodiorganosilanes with tetrahydrofuran in the presence of chloroplatinic acid.

Key words: chloro(4-chlorobutoxy)dimethylsilane, chloro(4-chlorobutoxy)(methyl)vinylsilane, chloro(4-chlorobutoxy)(methyl)phenylsilane, chloro(4-chlorobutoxy)(methyl)propylsilane, chloro(4-chlorobutoxy)(3-chloropropyl)methylsilane, chloro(4-chlorobutoxy)diphenylsilane, chloro(4-chlorobutoxy)diethylsilane, (4-chlorobutoxy)dimethyl(phenoxy)silane, (4-chlorobutoxy)trimethylsilane.

(Diorgano)chloro(4-chlorobutoxy)silanes and (diorgano)di(4-chlorobutoxy)silanes are of interest as intermediate products for the synthesis of diorganosilacyclohexanes, organo(4-hydroxybutyl)silanes, and organosilicon polyesters and polyurethanes on their base.

The derivatives of organo(4-chlorobutoxy)silanes were prepared by the etherification of dichlorodimethylsilane (DCDMS)[1—3], chlorotrimethylsilane,[1—8] ethyl(dimethyl)chlorosilane,[1] and various methyl(phenyl)chlorosilanes with 4-chlorobutanol; the effect of phenyl and methyl groups on the yield of the products was studied.[9] However, di(4-chlorobutoxy)dimethylsilane could not be isolated due to decomposition of the product.[1] The second method is based on the cleavage of tetrahydrofuran with different chlorosilanes. Thus, when alkyltrichlorosilanes or $SiCl_4$ were heated with THF in the presence of $ZnCl_2$, the corresponding (organo)dichloro(4-chlorobutoxy)silanes[10] and (dichloro)di(4-chlorobutoxy)silane and 1,4-dichlorobutane were obtained.[11] In contrast to organotrichlorosilanes, (dichloro)dimethylsilane and methyldichlorosilane cleave THF at both C—O bonds forming 1,4-dichlorobutane and polyorganosiloxane. Later, chloro(4-chlorobutoxy)dimethylsilane was synthesized by heating DCDMS with THF in an autoclave[12] to temperature ≤200 °C or at atmospheric pressure[13] in the presence of $ZnCl_2$. At temperatures above 200 °C, and also in an autoclave at 130—190 °C in the presence of pyridinium salts or $AlCl_3$ as well as without a catalyst, dihalobutanes were obtained.[14,15] When $SiCl_4$ is refluxed with THF in the presence of concentrated HCl, 4-chlorobutanol and a mixture of chloro(4-chlorobutoxy)silanes and 19 % of tetrakis(4-chlorobutoxy)silane were synthesized.[16] Heating of organochlorosilanes with THF and MgI_2 or $MgBr_2$ affords 4-iodobutoxy- or (4-bromobutoxy)organosilanes, respectively,[17] apparently, as a result of halide exchange at the silicon atom followed by the reaction of iodo- or bromosilanes thus formed with THF.

Chlorotrimethylsilane reacts with THF only in an autoclave at 160—170 °C, whereas bromotrimethylsilane reacts at 73—100 °C (see Ref. 18) and even at ambient temperature[18,19] when allowed to stay for a long time, and iodotrimethylsilane reacts rapidly at 60 and 25 °C forming[19] the corresponding (4-halobutoxy)trimethylsilanes. Previously, we have synthesized various (diorgano)alkoxy(4-chlorobutoxy)silanes and (diorgano)di(4-chlorobutoxy)silanes by the reaction of (dichloro)diorganosilanes with THF in the presence of alcohols at ambient temperature. The reaction proceeds over a long time.[21,22]

The aim of the present work is the preparation of (diorgano)chloro(4-chlorobutoxy)silanes by the reaction of (dichloro)diorganosilanes with THF at atmospheric pressure in the presence of various catalytic systems.

Various salts were studied as catalysts. When DCDMS was refluxed in THF in the presence of $AlCl_3$, $FeCl_3$, $ZnCl_2$, $SnCl_2$, the formation of 1,4-dichlorobutane was observed. Since these salts are active catalysts of the heterofunctional condensation of chlorosilanes with alkoxysilanes, (4-chlorobutoxy)silane formed reacts rapidly with the starting chlorosilane giving 1,4-dichlorobutane. In the presence of 0.2—0.3 % $BaCl_2$, $Al(OPr^i)_3$, $Cr(CO)_6$, $C_5H_5Mn(CO)_6$, or $PdCl_2$, the reaction practically was not completed over 20—30 h. When the mixture was refluxed in the presence of 0.25 % $RhCl_3$, only 30 % of chloro(4-chlorobutoxy)dimethylsilane (CBDMS) was obtained after 30 h and only in the presence of $H_2PtCl_6 \cdot 6H_2O$ or $Rh_4(CO)_{12}$, (dichloro)diorganosilanes cleave THF rapidly and smoothly (without apparent formation of 1,4-dichlorobutane). A mixture of DCDMS with THF remains unchanged for one month at ambient temperature without a catalyst. In Table 1, the effect of the amount of H_2PtCl_6 on the rate of the reaction of DCDMS with THF is given. As can be seen, substantial cleavage of THF occurs at a catalyst percentage of ≥0.08 %. At the molar ratio DCDMS : THF = 1 : 1,

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Table 1. Effect of the amount of H_2PtCl_6 on the rate of the reaction of DCDMS with THF and the yield of CBDMS

Amount of catalyst (%)	Reaction time /h	B.p. of the final mixture /°C	$[Cl_{titr}]$ (%) in the product	Yield of CBDMS (%)
0.02	12	70	36.5	0
0.25	2.5	112	20.9	79
0.04	22	74	34	0
0.08	20	83	28	20
0.1	12	109	18	61
0.15	5	110	16	61
0.15	2	105	21	68
0.2	2.5	106	21	62
0.22	1.5	112	20.9	75
0.25	2.5	106	20.8	84

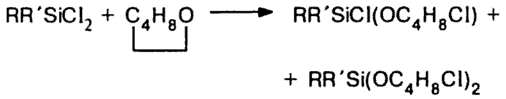
Table 2. Reaction conditions and properties of synthesized $RR'ClSi(OC_4H_8Cl)$

R	R′	Mass/g		Content of catalyst (%)	Time /h	Content of Cl_{titr}		Yield (%)	B.p. /°C(*p*/Torr)	n_D^{20}	d_4^{20}	Found Calculated (%)					Molecular formula
		R_2SiCl_2	THF			start.	final.					MR_D	C	H	Cl	Si	
Me	Ph	99.0	34.8	0.22	5	28.0	14.8	70	129—135 (2)	1.5035	1.1339	68.72 69.16	50.10 50.19	6.56 6.13	26.35 26.95	11.49 10.67	$C_{11}H_{16}Cl_2OSi$
Me	Vin*	91.0	40.0	0.15	16	33.4	25.0	51	103—106 (10)	1.4515	1.0745	53.41 53.50	39.28 39.44	6.53 6.61	33.12 33.26	13.02 13.17	$C_7H_{14}Cl_2OSi$
Me	Pr	62.0	25.5	0.22	4	33.0	18.8	74	114—117 (10)	1.4440	1.0410	58.64 58.60	41.05 41.93	7.87 7.91	31.30 30.94	12.19 12.26	$C_8H_{18}Cl_2OSi$
Et	Et	82.0	36.0	0.20	19	31.6	24.9	39	121—123 (10)	1.4475	1.0534	58.19 58.36	41.70 41.93	8.26 7.91	30.60 30.94	12.33 12.26	$C_8H_{18}Cl_2OSi$
Ph	Ph	113	32.0	0.14	4	27.0	13.0	61	192—198 (2)	1.5520	1.1700	88.94 88.98	58.82 59.07	5.59 5.58	22.50 21.80	8.91 8.63	$C_{16}H_{18}Cl_2OSi$
Me	ClPr**	34.0	12.0	0.2	5	19.5	15.0	78	158—164 (10)	1.4650	1.1480	63.54 63.44	34.82 36.44	6.23 6.50	39.63 40.35	10.22 10.65	$C_8H_{17}Cl_3OSi$

* Vin — vinyl. ** ClPr — 3-chloropropyl.

along with CBDMS, di(4-chlorobutoxy)dimethylsilane (DCBDM) is formed, the yield of which decreases with the increase in molar percentage of DCDMS. Other (dichloro)diorganosilanes react similarly (Table 2).

The reaction proceeds as follows:



$$RR'SiCl_2 + C_4H_8O \longrightarrow RR'SiCl(OC_4H_8Cl) + RR'Si(OC_4H_8Cl)_2$$

In the presence of H_2PtCl_6, chlorotriorganosilanes react with THF as well as (dichloro)diorganosilanes, in particular, chlorotrimethylsilane and chlorodimethyl(phenoxy)silane, affording the corresponding triorgano(4-chlorobutoxy)silanes.

In Table 2, the reaction conditions and the properties of newly synthesized chloro(4-chlorobutoxy)diorganosilanes are presented.

Experimental

Effect of the amount of H_2PtCl_6 on the time of reaction of DCDMS with THF. The catalyst was added to a mixture of DCDMS and THF (1 : 0.86, Cl_{titr} 37—38 %) (50—70 g); the mixture was refluxed, and the percentage of titrated chlorine and the boiling point of the reaction mixture were measured in the course of the reaction. The data obtained are presented in Table 1.

Chloro(4-chlorobutoxy)dimethylsilane and di(4-chlorobutoxy)dimethylsilane. A mixture of DCDMS (63 g) and THF (54 g) was refluxed for 6 h in the presence of H_2PtCl_6 (0.16 %) (a 19 % solution in Pr^iOH); the temperature of the reaction mixture increased from 68 to 105 °C and the percentage of titrated chlorine decreased from 29.7 to 16 %. CBDMS (57 g, 58 %) and DCBDM (7.5 g, 9 %) were isolated by fractional distillation. CBDMS, b.p. 105—110 °C/20 Torr. Found (%): Cl_{titr}, 17.4; Cl_{total}, 34.8. $C_6H_{14}Cl_2OSi$. Calculated (%): Cl_{titr}, 17.66; Cl_{total}, 35.3]. DCBDM, b.p. 109—111 °C/2 Torr, n_D^{20} 1.4465, d_4^{20} 1.0582. Found (%): C, 43.24; H, 7.81; Si, 10.28; Cl, 25.79. $C_{10}H_{22}Cl_2O_2Si$. Calculated (%): C, 43.95; H, 8.11; Cl, 25.95; Si, 10.28.

Literature data: CBDMS, b.p. 64 °C/4.2 Torr,[12] 62 °C/4 Torr,[13] 92—95 °C/16 Torr;[22] DCBDM, b.p. 117—121 °C/1.5 Torr,[2] 105—112 °C/1.5 Torr,[3] 154—156 °C/15 Torr, n_D^{20} 1.4480, d_4^{20} 1.057.[22]

A portion of a mixture of DCDMS (216.5 g), THF (112 g), and 0.21 % of $RhCl_3 \cdot 4H_2O$ (48 g) was refluxed. B.p. of the starting mixture was 69 °C, Cl_{titr} 35.2 %; after 14 h, b.p. 77 °C, Cl_{titr} 30.9 %, and after 38 h, b.p. 100 °C, Cl_{titr} 22 %. CBDMS (15 g, 30 %), b.p. 56—62 °C/2 Torr, n_D^{20} 1.4368, Cl_{titr} 17.3 %, and $ClMe_2SiOSiMe_2(OC_4H_8Cl)$ (10.5 g) with an admixture of DCBDM, b.p. 105—115 °C, n_D^{20} 1.4440, Cl_{titr} 14.0 %, were isolated by fractional distillation.

A mixture of DCDMS and THF was refluxed in the presence of 0.2 % of rhodium carbonyl; the b.p. of the reaction mixture increased to 108 °C after 3 h. The yield of CBDMS was 59 %.

(4-Chlorobutoxy)dimethyl(phenoxy)silane. A mixture of dimethyl(phenoxy)chlorosilane (97 g), THF (35 g), and 0.25 % H_2PtCl_6 was heated at 130 °C for 9 h. The percentage of Cl_{titr} decreased to 3.6 %. (4-Chlorobutoxy)dimethyl(phenoxy)silane (50 g, 41 %) was isolated by fractional distillation, b.p. 155—160 °C/10 Torr, n_D^{20} 1.4865. Found (%): Cl, 13.6. $C_{12}H_{19}ClO_2Si$. Calculated (%): Cl, 13.76. Literature data:[22] b.p. 141—150 °C/7 Torr, n_D^{20} 1.4860.

(4-Chlorobutoxy)trimethylsilane. A mixture of Me_3SiCl (31 g), THF (14 g), and 0.2 % H_2PtCl_6 was heated at 65 °C for 10 h, (4-chlorobutoxy)trimethylsilane (10 g, 25 %) was obtained, b.p. 75—78 °C/13 Torr, n_D^{20} 1.4240, d_4^{22} 0.9260, MR_{found} 49.78, MR_{calc} 49.80. Literature data:[18] b.p. 74.5—75 °C/19 Torr, n_D^{20} 1.4270, d_4^{20} 0.9354.

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