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Abstract

Full Text

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REACTIONS OF SUBSTITUTION OF CHLORINE BY ALKOXY GROUPS IN DICHLOROMETHYLDIMETHY LANE AND BIS(CHLOROMETHYL)METHYLCHLOROSILANE

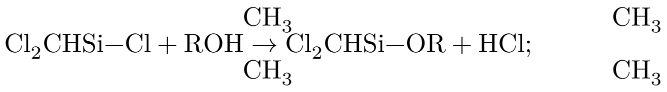
Reactions of substitution of a halide by alkoxy groups in alkyl- and arylchlorosilanes proceed readily, with the formation of alkyl- and arylalkoxysilanes (^{1,2}). α-Chloroethylchlorosilanes and α-chloromethylchlorosilanes react with alcohols to form α-chloroalkylalkoxysilanes ($^{3-5}$).

We considered it of interest to study the substitution of chlorine at the silicon atom by alkoxyl groups under the action of alcohols on dichloromethyldimethylchlorosilane and bis(chloromethyl)methylchlorosilane. It is known that an increase in the number of chlorine atoms in the α-position to the silicon atom sharply increases the lability of the C—Si bond; in trichloromethyltrichlorosilane it is destroyed on hydrolysis with water:

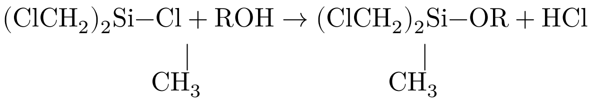
$$Cl_3CSiCl_3 + 4H_2O \rightarrow Si(OH)_4 + 3HCl + HCCl_3.$$

Consequently, one might have expected cleavage of the Si—C bond under conditions of the direct action of an alcohol on dichloromethyldimethylchlorosilane and bis(chloromethyl)methylchlorosilane, when, along with hydrogen chloride, water is also liberated (when hydrogen chloride acts on the alcohol), which could cause splitting off of the Cl_2CH-group. This should have affected the yields of dichloromethyldimethylalkoxysilanes and bis(chloromethyl)methylalkoxysilanes. The study of the reaction of chlorine substitution in dichloromethyldimethylchlorosilane and bis(chloromethyl)methylchlorosilane was carried out using ethyl, isopropyl, *n*-butyl, and isoamyl alcohols.

The experiments showed that, in the reaction of dichloromethyldimethylchlorosilane and bis(chloromethyl)methylchlorosilane with alcohols under the experimental conditions, no splitting off of the Cl_2CH-group was observed, and the reactions proceed according to the schemes:



$$Cl_2CH\overset{CH_3}{\underset{CH_3}{Si}}{-}Cl + ROH \rightarrow Cl_2CH\overset{CH_3}{\underset{CH_3}{Si}}{-}OR + HCl;$$



$$(ClCH_2)_2\underset{\displaystyle CH_3}{\underset{|}{Si}}-Cl + ROH \rightarrow (ClCH_2)_2\underset{\displaystyle CH_3}{\underset{|}{Si}}-OR + HCl$$

In this process, dichloromethyldimethylalkoxysilanes and bis(chloromethyl)methylalkoxysilanes are obtained in high yields, comparable with the yields of chloromethyldimethylalkoxysilanes.

Consequently, under the experimental conditions, i.e., in a strongly acidic medium, destruction of the Si–C bond is not observed in dichloromethyldimethylchlorosilane or in bis(chloromethyl)methylchlorosilane. By means of the reaction indicated above, new compounds were obtained, the properties of which are given in Table 1.

Table 1

Substance	Chemical formula	B.p., °C	Pressure in mm Hg	Yield in %	d_4^{20}	n_D^{20}	MR_D, calcd.	MR_D, found
Chloromethyldimethylmethoxysilane	$ClCH_2(CH_3)_2SiOCH_3$	116.5–117	750	30	0.9890	1.4310	35.84	35.59
Chloromethyldimethylethoxysilane	$ClCH_2(CH_3)_2SiOC_2H_5$	131.5	745	79	0.9512	1.4185	40.41	40.20
Chloromethyldimethylisopropoxysilane	$ClCH_2(CH_3)_2SiOC_3H_7$	144.5	750	—	0.9473	1.4192	45.13	—
Chloromethyldimethyl-*n*-butoxysilane	$ClCH_2(CH_3)_2SiOC_4H_9$	37–38	3	73	0.9406	1.4262	49.77	49.36
Chloromethyldimethylisoamyloxysilane	$ClCH_2(CH_3)_2SiOC_5H_{11}$	38–40	1	64	0.9118	1.4270	54.42	54.40
Dichloromethyldimethylethoxysilane	$Cl_2CH(CH_3)_2SiOC_2H_5$	62–63	10	67	1.0880	1.4402	45.33	45.07
Dichloromethyldimethylisopropoxysilane	$Cl_2CH(CH_3)_2SiOC_3H_7$	176	750	65	1.0778	1.4412	49.98	49.41
Dichloromethyldimethyl-*n*-butoxysilane	$Cl_2CH(CH_3)_2SiOC_4H_9$	73–74	5	60	1.0480	1.4450	54.63	54.34
Dichloromethyldimethylisoamyloxysilane	$Cl_2CH(CH_3)_2SiOC_5H_{11}$	47–48	2	82	1.0297	1.4458	59.28	59.39
Bis(chloromethyl)methylethoxysilane	$(ClCH_2)_2CH_3SiOC_2H_5$	40	2	76	1.1198	1.4512	45.33	44.71
Bis(chloromethyl)methyl-*n*-butoxysilane	$(ClCH_2)_2CH_3SiOC_4H_9$	62–64	2	84	1.0681	1.4515	54.63	54.19
Bis(chloromethyl)methylisoamyloxysilane	$(ClCH_2)_2CH_3SiOC_5H_{11}$	116–118	16	75	1.0551	1.4522	59.28	58.55

Experimental Part

α-Chloromethyldimethylmethoxysilane. Into a flask equipped with a reflux condenser, dropping funnel, thermometer, and stirrer were placed 100 g

(0.7 mole) of chloromethyldimethylchlorosilane (b.p. 114–114.5°; Cl, by Folgard, 25.12%) and 110 g (0.74 mole) of diethylaniline (b.p. 214°). The mixture was heated and stirred. Upon reaching a temperature of 60°, 32 g (1 mole) of methyl alcohol (b.p. 64°) was added over 2 hours. After all the alcohol had been introduced, the reaction mixture was stirred at 60–70° for half an hour. After cooling, the precipitate formed, which was diethylaniline hydrochloride, was separated. The filtrate was distilled from a Favorskii flask. After a second distillation, a product with b.p. 116–117° was obtained. There were obtained 29 g of chloromethyldimethylmethoxysilane with b.p. 116.5–117°; n_D^{20} 1.4310; d_4^{20} 0.9890; yield 30%.

Found, %: C 35.01; 34.87; H 8.03; 8.33; Cl 25.19; 25.32; Si 18.79; 19.72
$C_4H_{11}OClSi$. Calculated, %: C 34.64; H 7.92; Cl 25.57; Si 20.25

α-Chloromethyldimethyl-n-butoxysilane. Obtained analogously from 71.5 g (0.5 mole) of chloromethyldimethylchlorosilane (b.p. 114–114.5°; Cl, by Folgard, 25.12%) and 50 g (0.67 mole) of n-butyl alcohol (b.p. 116°, n_D^{20} 1.4008). The resulting product was distilled under vacuum from

Claisen flask. 65.8 g of chloromethyldimethylbutoxysilane were obtained, b.p. 37-38°/3 mm; n_D^{20} 1.4262; d_4^{20} 0.9406; yield 73%.

Found, %: C 46.25; 46.11; H 9.20; 9.07; Cl 19.20; 19.38; Si 15.25; 15.34
$C_7H_{17}OClSi$. Calculated, %: C 46.51; H 9.47; Cl 19.61; Si 15.54

α-Chloromethyldimethyl-(iso)-amyloxysilane. Prepared analogously from 40 g (0.28 mole) of chloromethyldimethylchlorosilane (b.p. 114–114.5°; Cl, by Follgard, 25.12%) and 30 g (0.34 mole) of isoamyl alcohol (b.p. 132°, n_D^{20} 1.4090). The product was distilled in vacuo from a Claisen flask. 35 g of chloromethyldimethyl-(iso)-amyloxysilane were obtained, b.p. 38–40°/1 mm; n_D^{20} 1.4270; d_4^{20} 0.9118; yield 64%.

Found, %: C 49.72; 49.80; H 9.69; 9.43; Cl 17.83; 18.01; Si 14.20; 14.47
$C_8H_{19}OClSi$. Calculated, %: C 49.33; H 9.83; Cl 18.20; Si 14.42

Dichloromethyldimethylethoxysilane. Prepared analogously from 133 g (0.75 mole) of dichloromethyldimethylchlorosilane (b.p. 148°; Cl, by Follgard, 20.32%) and 50 g (1.1 mole) of absolute ethyl alcohol. The resulting product was distilled in vacuo from a Claisen flask. 94 g of dichloromethyldimethylethoxysilane were obtained, b.p. 62–63°/10 mm; n_D^{20} 1.4402; d_4^{20} 1.0880; yield 67%.

Found, %: C 32.48; 32.36; H 6.51; 6.31; Cl 37.70; 38.34; Si 15.31; 15.2
$C_5H_{12}OCl_2Si$. Calculated, %: C 32.09; H 6.46; Cl 37.88; Si 14.95

Dichloromethyldimethyl-(iso)-propoxysilane. Prepared analogously from 35 g (0.2 mole) of dichloromethyldimethylchlorosilane (b.p. 148°; Cl, by Follgard, 20.32%) and 15 g (0.25 mole) of isopropyl alcohol (b.p. 83°, n_D^{20} 1.3792). The product was distilled from a Favorsky flask. 26 g of dichloromethyldimethyl-(iso)-propoxysilane were obtained, b.p. 176°; n_D^{20} 1.4412; d_4^{20} 1.0778; yield 65%.

Found, %: C 35.71; 35.92; H 6.65; 6.86; Cl 36.01; 35.82; Si 14.38; 14.4
$C_6H_{14}OCl_2Si$. Calculated, %: C 35.82; H 7.01; Cl 35.24; Si 13.96

Dichloromethyldimethyl-*n*-butoxysilane. Prepared analogously from 52 g (0.29 mole) of dichloromethyldimethylchlorosilane (b.p. 148°; Cl, by Follgard, 20.32%) and 25 g (0.34 mole) of *n*-butyl alcohol (b.p. 116°; n_D^{20} 1.4008). The product was distilled in vacuo from a Claisen flask. 37 g of dichloromethyldimethylbutoxysilane were obtained, b.p. 73-74°/5 mm; n_D^{20} 1.4450; d_4^{20} 1.0480; yield 60%.

Found, %: C 39.22; 39.30; H 7.51; 7.81; Cl 32.35; 32.58; Si 12.38; 12.78
$C_7H_{16}OCl_2Si$. Calculated, %: C 39.06; H 7.48; Cl 32.95; Si 13.05

Dichloromethyldimethyl-(iso)-amyloxysilane. Prepared analogously from 35 g (0.2 mole) of dichloromethyldimethylchlorosilane (b.p. 148°; Cl, by Follgard, 20.32%) and 20 g (0.23 mole) of isoamyl alcohol (b.p. 132°; n_D^{20} 1.4090). The product was distilled in vacuo from a Claisen flask. 37 g of dichloromethyldimethyl-(iso)-amyloxysilane were obtained, b.p. 47-48°/2 mm; n_D^{20} 1.4458; d_4^{20} 1.0297; yield 82%.

Found, %: C 42.22; 42.49; H 7.54; 7.98; Cl 30.75; 30.35; Si 11.84; 11.96
$C_8H_{18}OCl_2Si$. Calculated, %: C 41.91; H 7.91; Cl 30.93; Si 12.25

Bis(chloromethyl)methylethoxysilane. Prepared analogously from 40 g (0.22 mole) of bis(chloromethyl)methylchlorosilane (b.p. 170°; Cl, by Follgard, 20.22%) and 20 g (0.43 mole) of absolute ethyl alcohol. The product was distilled in vacuo from a Claisen flask. 32 g of bis(chloromethyl)methylethoxysilane were obtained, b.p. 40°/2 mm; n_D^{20} 1.4512; d_4^{20} 1.1198; yield 76%.

Found, %: C 32.23; 32.01; H 6.50; 6.29; Cl 37.38; 37.75; Si 14.35; 14.38
$C_5H_{12}OCl_2Si$. Calculated, %: C 32.09; H 6.46; Cl 37.88; Si 14.95

Bis(chloromethyl)methyl-*n*-butoxysilane. Obtained analogously from 35 g (0.2 mole) of bis(chloromethyl)methylchlorosilane (b.p. 170°; Cl, by Folgard, 20.22%) and 25 g (0.34 mole) of *n*-butyl alcohol (b.p. 116°, n_D^{20} 1.4008). The product was distilled in vacuo from a Claisen flask. 36 g of bis(chloromethyl)methylbutoxysilane was obtained, b.p. 62-64°/2 mm; n_D^{20} 1.4515; d_4^{20} 1.0681; yield 84%.

Found, %: C 39.34; 39.50; H 7.05; 7.52; Cl 32.31; 32.83; Si 12.68; 12.74
$\mathrm{C_7H_{16}OCl_2Si}$. Calculated, %: C 39.06; H 7.48; Cl 32.95; Si 13.05

Bis(chloromethyl)methyl-(iso)-amyloxysilane. Obtained analogously from 35 g (0.2 mole) of bis(chloromethyl)methylchlorosilane (b.p. 170°; Cl, by Folgard, 20.22%) and 20 g (0.23 mole) of isoamyl alcohol (b.p. 132°, n_D^{20} 1.4090). The product was distilled from a Claisen flask. 34 g of bis(chloromethyl)methyl-(iso)-amyloxysilane was obtained, b.p. 116-118°/16 mm; n_D^{20} 1.4522; d_4^{20} 1.0551; yield 75%.

Found, %: C 41.34; 41.62; H 7.96; 8.34; Cl 30.98; 30.61; Si 11.93; 11.63
$\mathrm{C_8H_{18}OCl_2Si}$. Calculated, %: C 41.91; H 7.91; Cl 30.93; Si 12.25

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