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Abstract

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THE CHLOROMETHYLATION REACTION OF ARYLALIPHATIC DISILOXANES

SYNTHESIS OF CHLOROMETHYLBENZYLDIMETHYLCHLOROSILANE AND ITS DERIVATIVES

The chloromethylation reaction of aromatic hydrocarbons has been studied in detail by a number of investigators ($^{1-6}$). The chloromethylation of organosilicon compounds was first carried out by A. V. Topchiev and N. S. Nametkin with co-workers (^{7}), who synthesized chloromethylbenzyltrimethylsilane by the action of 35% formaldehyde on trimethylbenzylsilane in an aqueous medium or in carbon tetrachloride at 40–50° in the presence of zinc chloride. Our investigations have shown that the chloromethylation reaction of a benzyl group bonded to silicon can be successfully used for the synthesis of chloromethylbenzyldimethylchlorosilane. The chloromethylation of benzyldimethylchlorosilane was carried out by us according to the following scheme:

$$C_6H_5CH_2(CH_3)_2SiCl + HCHO + HCl \rightarrow ClCH_2C_6H_4CH_2(CH_3)_2SiCl + H_2O.$$

As our investigations showed, this reaction proceeds well without a catalyst in fuming hydrochloric acid, using paraform as the chloromethylating agent.

When chloromethylation is carried out in the presence of zinc chloride, the reaction is accompanied by secondary processes that lead to the formation of viscous, non-distillable products containing diphenylmethane groupings, according to the scheme:

$$\begin{aligned}
&C_6H_5CH_2(CH_3)_2SiCl + HCHO + HCl \xrightarrow{ZnCl_2}\\
&\rightarrow ClCH_2C_6H_4CH_2(CH_3)_2SiCl + H_2O + C_6H_5CH_2(CH_3)_2SiCl \xrightarrow{ZnCl_2}\\
&\rightarrow ClSi(CH_3)_2CH_2C_6H_4CH_2C_6H_4CH_2(CH_3)_2SiCl + H_2O \rightarrow\\
&\rightarrow [-O - Si(CH_3)_2 - CH_2 - C_6H_4 - CH_2 - C_6H_4 - CH_2 - Si(CH_3)_2-]_n .
\end{aligned}$$

Isolation of pure chloromethylbenzyldimethylchlorosilane from the reaction mixture was accomplished by hydrolysis of the reaction products with an excess of water, followed by cleavage of the mixture of disiloxanes with concentrated sulfuric acid in the presence of ammonium chloride according to the scheme:

$$2ClCH_2C_6H_4CH_2(CH_3)_2SiCl + H_2O \rightarrow (ClCH_2C_6H_4CH_2(CH_3)_2Si)_2O + 2HCl$$

$$(ClCH_2C_6H_4CH_2(CH_3)_2Si)_2O + 2H_2SO_4 + 2NH_4Cl \rightarrow$$

$$\rightarrow 2ClCH_2C_6H_4CH_2(CH_3)_2SiCl + 2NH_4HSO_4 + H_2O.$$

The overall yield of chloromethylbenzyldimethylchlorosilane, calculated on the reacted benzyldimethylchlorosilane, was 60% of the amount that entered

into the reaction, or 30% of that introduced. Attempts to isolate chloromethylbenzyldimethylchlorosilane or the corresponding disiloxane by direct distillation under vacuum of the chloromethylation products washed with water led to lower yields, since in this case it was difficult to fractionate the reaction mixture, probably because of the formation of mixed disiloxanes according to the scheme:

$$ClCH_2C_6H_4CH_2(CH_3)_2SiCl + C_6H_5CH_2(CH_3)_2SiCl + H_2O \rightarrow$$

$$\rightarrow ClCH_2C_6H_4CH_2(CH_3)_2SiOSi(CH_3)_2CH_2C_6H_5 + 2HCl.$$

Investigation of chloromethylbenzyldimethylchlorosilane in order to study its properties showed that it possesses all the properties of haloalkylchlorosilanes. On hydrolysis with water it readily forms a disiloxane according to the scheme:

$$2ClCH_2C_6H_4CH_2(CH_3)_2SiCl + H_2O \rightarrow (ClCH_2C_6H_4CH_2(CH_3)_2Si)_2O + 2HCl$$

As a result of this reaction, bis(chloromethylbenzyl)tetramethyldisiloxane was isolated. On treatment of bis(chloromethylbenzyl)tetramethyldisiloxane with potassium acetate in acetic acid medium, bis(acetoxymethylbenzyl)tetramethyldisiloxane was obtained

$$(ClCH_2C_6H_4CH_2(CH_3)_2Si)_2O + 2CH_3COOK \rightarrow (CH_3COOCH_2C_6H_4CH_2(CH_3)_2Si)_2O + 2KCl.$$

On hydrolysis of bis(acetoxymethylbenzyl)tetramethyldisiloxane with aqueous-alcoholic alkali, cleavage of the acetate group occurs with formation, in the first stage, of bis(oxymethylbenzyl)tetramethyldisiloxane, which subsequently decomposes as a result of the catalytic action of the alkali and during distillation, probably with formation of toluyl alcohol and polydimethylsiloxanes with terminal functional groups according to the scheme:

$$(CH_3COOCH_2C_6H_4CH_2(CH_3)_2Si)_2O + 2NaOH \rightarrow$$

$$\rightarrow 2CH_3COONa + (HOCH_2C_6H_4CH_2(CH_3)_2Si)_2O \xrightarrow{NaOH+H_2O}$$

$$\rightarrow HOCH_2C_6H_4CH_2(CH_3)_2Si(OSi(CH_3)_2)_{nCH}2C_6H_4CH_2OH + CH_3C_6H_4CH_2OH.$$

The properties of the synthesized products are given in Table 1.

Experimental Part

The following were used in the work: benzyldimethylchlorosilane, b.p. 72–73°/7 mm, synthesized by the method described by us earlier (8), commercial paraform, and chemically pure concentrated hydrochloric acid.

Chloromethylation of benzyldimethylchlorosilane. A reaction flask equipped with a stirrer, thermometer, and reflux condenser was charged with 55.5 g (0.3 mole) of benzyldimethylchlorosilane, 10 g (0.3 mole) of paraform, and 100 ml of chemically pure conc. hydrochloric acid. The reaction mixture was heated to 60° and, with vigorous stirring for 4–5 h, hydrogen chloride was passed into the reaction mixture. The reaction product was then cooled, and the upper layer, containing chloromethylbenzyldimethylchlorosilane, was separated from the reaction mixture.

Hydrolysis of the chloromethylation products. A separatory funnel was charged with 250 ml of water and a small amount of ice; the reaction mass obtained in the preceding experiment was introduced into the funnel with vigorous stirring. After completion of the hydrolysis, ether was added to the mixture and the ether layer was separated from the aqueous layer; the latter was extracted once with ether, and the combined ether layer was washed with water and dried with sodium sulfate. After removal of the ether, 60 g of a liquid product containing unpurified bis(chloromethylbenzyl)tetramethyldisiloxane was obtained.

Chloromethylbenzyldimethylchlorosilane. Into a flask were placed 24 g (0.45 mole) of ammonium chloride and 60 g (0.14 mole) of bis-(chloromethylbenzyl)-tetramethyldisiloxane, obtained in the preceding experiment. With stirring and cooling with ice, sulfuric acid (sp. gr. 1.84) was introduced into the mixture in an amount of 60 g (0.6 mole). After the addition of sulfuric acid was complete, the mixture was stirred for another 15–20 min; then the liquid phase was decanted from the precipitate of ammonium sulfate, separated from the lower layer of sulfuric acid, and the reaction product was distilled in vacuo. This gave 26 g of chloromethylbenzyldimethylchlorosilane with b.p. 133°/5 mm;

d_4^{20} 1.1139, n_D^{20} 1.5234, MR found 63.96; calculated 63.62.

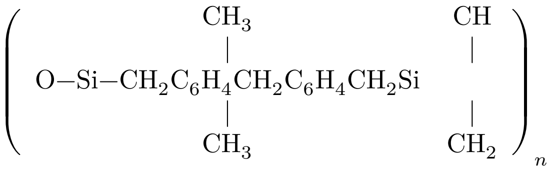
Found, %:	C 51.60; 51.56;	H 6.26; 6.20;	Si 12.53; 12.40;	Cl 29.27; 29.12
$C_{10}H_{14}SiCl_2$. Calculated, %:	C 51.55;	H 6.05;	Si 12.03;	Cl 30.40

5 and c-(chloromethylbenzyl)-tetramethyldisiloxane. Into a separatory funnel were placed 100 ml of water and, with vigorous stirring, 46.6 g (0.2 mole) of chloromethylbenzyldimethylchlorosilane was introduced in small portions. After completion of hydrolysis, the ether layer was separated from the aqueous layer, washed with water, and dried over sodium sulfate. Then, after removal of the solvent, the reaction product was distilled in vacuo. This gave 22 g of bis-(chloromethylbenzyl)-tetramethyldisiloxane with b.p. 232°/5 mm; d_4^{20} 1.0917; n_D^{20} 1.5275; MR found 115.90; calculated 116.34.

Found, %:	C 58.84; 58.20;	H 7.03; 7.33;	Si 13.47; 13.70;	Cl 17.48
$C_{20}H_{28}Si_2Cl_2O$. Calculated, %:	C 58.38;	H 6.85;	Si 13.63;	Cl 17.23

Chloromethylation of benzyldimethylchlorosilane in the presence of zinc chloride. Into a reaction flask equipped with a thermometer, stirrer, and reflux condenser were placed 55.5 g (0.3 mole) of benzyldimethylchlorosilane, 10 g (0.3 mole) of paraform, 5 g of zinc chloride, and 100 ml of concentrated hydrochloric acid. The reaction mixture was heated to 60-70°, and, with vigorous stirring, hydrogen chloride was passed through the mixture for 4-5 hr. Then, after cooling, the upper layer containing the chloromethylated product was separated from the reaction mixture and subjected to hydrolysis by the procedure described above.

When an attempt was made to fractionate the hydrolysis product in vacuo, the reaction mass, on heating, turned into a viscous nondistillable polymer:



$$\left(\mathrm{O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_2C_6H_4CH_2C_6H_4CH_2\underset{CH_2}{\overset{CH}{Si}}} \right)_n$$

Found, %:	C 68.93; 68.70;	H 8.26; 8.16;	Si 16.62; 16.77,
Calculated, %:	C 69.88;	H 8.02;	Si 17.19

Bis-(acetoxymethylbenzyl)-tetramethyldisiloxane. Into a reaction flask were placed 21 g (0.05 mole) of bis-(chloromethylbenzyl)-tetramethyldisiloxane, 12.01 g (0.1 mole) of anhydrous potassium acetate, and 100 ml of glacial acetic acid. The reaction mixture was stirred for 10 hr at 118–120°, after which the reaction product was filtered from potassium chloride, the filtrate was washed free of acetic acid with water, dried over sodium sulfate, and, after removal of the solvent, the reaction product was distilled in vacuo. This gave 15 g of bis-(acetoxymethylbenzyl)-tetramethyldisiloxane with b.p. 268–270°/5 mm; d_4^{20} 1.0622; n_D^{20} 1.5130; MR found 129.76; calculated 129.01.

Found, %: C 62.63; 62.45; H 7.55; 7.49; Si 12.92; 12.15; $OCOCH_3$ 25.34; 25.20
$C_{24}H_{34}Si_2O_5$. Calculated, %: C 62.84; H 7.47; Si 12.32; $OCOCH_3$ 25.74

Table 1

Product name	b.p., °C/mm	d_4^{20}	n_D^{20}	MR, found	MR, calc.	C found, %	C calc., %	H found, %	H calc., %	Si found, %	Si calc., %	Cl found, %	Cl calc., %
Chloromethylbenzyldimethylchlorosilane $ClCH_2C_6H_4CH_2Si(CH_3)_2Cl$	133°/5	1.1139	1.5234	63.96	63.62	51.60; 51.56	51.55	6.26; 6.20	6.05	12.53; 12.40	12.03	29.12; 29.27	30.40
Bis-(chloromethylbenzyl)-tetramethyldisiloxane $(ClCH_2C_6H_4CH_2Si(CH_3)_2)_2O$	232°/5	1.0947	1.5275	115.90	116.34	58.84; 58.20	58.38	7.03; 7.33	6.85	13.47; 13.70	13.63	17.48	17.23
Bis-(acetoxymethylbenzyl)-tetramethyldisiloxane $(CH_3COOCH_2C_6H_4CH_2Si(CH_3)_2)_2O$	268–270°/5	1.0622	1.5130	129.76	129.01	62.63; 62.45	62.84	7.55; 7.49	7.47	12.92; 13.15	12.32	25.34; 25.20	25.74

Hydrolysis of bis-(acetoxymethylbenzyl)-tetramethyldisiloxane. Into a reaction flask were placed 13 g (0.028 mole) of bis-(acetoxymethylbenzyl)-tetramethyldisiloxane, 3.01 g (0.056 mole) of caustic potassium, 30 g of freshly distilled ethyl alcohol, and the reaction mixture was boiled with a reflux condenser for one hour; then the reaction product was transferred to a separatory funnel, washed with water, and dried with sodium sulfate. During distillation under vacuum, partial decomposition of the product and a noticeable increase in the viscosity of the still residue were observed.

In a second experiment, the still residue after removal of the solvent and volatile substances under vacuum was analyzed.

Found, %: C 59.88; 60.06; H 8.23; 8.32; Si 18.15; 17.98; OH 6.24; 6.21.

* For bis-(oxymethylbenzyl)-tetramethyldisiloxane the calculated content of C, H, Si, and OH groups is, in percent: C 64.12; H 8.07; Si 14.98 and OH 9.07, whereas for the trimer of the formula

$$HOCH_2C_6H_4CH_2Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2CH_2C_6H_4CH_2OH$$

the calculated elemental content is C 58.88; H 8.08; Si 18.76 and OH 7.57. The data obtained indicate that the hydrolysis product of bis-(acetoxymethylbenzyl)-tetramethyldisiloxane is close to the trimer in its elemental composition.

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Note: Figure translations are in progress. See original paper for figures.

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