REACTION OF TETRAMETHYLDIHYDRODISILOXANE WITH CHLORAL HYDRATE

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In [1], the preparation of cyclic siloxanes containing some heteroatoms in the ring is described:



In the present article, we report the results of studies of the reaction of tetramethyldihydrodisiloxane (TMDS) with chloral hydrate (ChH) undertaken to obtain a similar cyclic product.

The mixture (1:1) of TMDS and ChH reacted exothermically with an induction period of 20-30 min. The main reaction product of ChH was trichloroethyl alcohol (TCEA), in a yield of up to 90 mole%, and 5 mole% CHCl₃ was also found. Among the organosilicon products, we found linear polysiloxanes with the general formula $H(CH_3)_2Si[OSi(CH_3)_2]_nOSi(CH_3)_2H$, where n = 1, 2, and 3. Their yields were (in moles per 1 mole of TMDS) 0.27 for n = 1, 0.06 for n = 2, and 0.09 for n = 3. According to the data of [2], ChH can be converted to a mixture of trichloro- and dichloroethyl alcohols in the presence of a silicon-containing substance of general composition $Si_6H_6O_3$.

Organosilicon hydrides can undergo addition to the CO group of aldehydes with the formation of moisture-sensitive organosilicon alkoxy compounds. Since stable hydrates of some aldehydes (chloral, glyoxylic acid) behave like aldehydes in reactions [3], it can be assumed that TMDS reacts with ChH as with chloral, and the bound water acts as a hydrolyzing agent. We obtained a product of the addition of TMDS to chloral. Without isolating it, we subjected it to hydrolysis. TCEA, as the main chlorine-containing product, was isolated in good yield. The high yield and the simplicity of the synthesis and isolation of TCEA make the reaction of TMDS with ChH convenient for preparative purposes.

To find conditions for obtaining the above-mentioned cyclic compound, we intended to carry out the reaction of TMDS with ChH in the presence of catalysts $(H_2PtCl_6 \text{ and }PdCl_2)$. There are no data on the catalytic activity of PdCl₂ with respect to TMDS, and H_2PtCl_6 has been considered to be a catalyst not causing condensation of hydrosiloxanes [4].

It was found that $PdCl_2$ or H_2PtCl_6 , taken in an amount 2% of the weight of TMDS, catalyzed siloxane condensation at 20°C in an ether solution. The gas phase which formed with both catalysts consisted of dimethylsilane (~0.20 mole per 1 mole of reacted TMDS) and traces of hydrogen. Linear polysiloxanes of the indicated general formula with n = 1, 2, and 3 were identified in the liquid phase. Their yields in the presence of $PdCl_2$ or H_2PtCl_6 were equal (in moles per 1 mole of reacted TMDS) to 0.35 or 0.13 for n = 1, 0.08 or 0.03 for n = 2, and traces or 0.01 for n = 3, respectively. The obtained results are explained by the scheme proposed in [5]:

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TABLE 1

NO.	: ratio of S to ChH	Reaction conditions	Degree of conver- sion of TMDS, ϕ_0	Products					
				in moles per 1 mole of reacted TMDS				in moles per 1 mole of ChH	
				(CH₅)₂SiH₂	$H(CH_3)_2Si[OSi(CH_3]_2]_nOSi(CH_3)_2H$				
ry hr	Mole				<i>n</i> = 1	n=2	n = 3	CCI ₃ CH(OH) ₂	CIICI
L	1:2	20°, 4 h,	70	0,02	0,37	0,06	0,01	0,59	0,35
3	1:1 2:1 4:1	20°, 4 h 80°, 30 min 80°, 30 min	70 75 75	0,02 Traces "	0,34 0,33 0,48	0,05 0,09 0,01	0,03 0,02 Traces	0,50 0,35 0,03	$0,48 \\ 0,65 \\ 0,94$

$$\begin{split} & H(CH_3)_2 SiOSi(CH_3)_2 H \xrightarrow{Ct} (CH_3)_2 SiH_2 + [(CH_3)_2 Si = 0] \\ & H(CH_3)_2 SiOSi(CH_3)_2 H \xrightarrow{\pi[(CH_3)_2 Si = 0]} H(CH_3)_2 Si[OSi(CH_3)_2]_n OSi(CH_3)_2 H \end{split}$$

The solution of ChH in ether did not change for many days during standing over PdCl₂ or H₂PtCl₆. However, when TMDS was added, the reaction involving ChH began immediately. This process was carried out with different mole ratios of the reagents (Table 1).

From Table 1, it is evident that the main product of the reaction of ChH was $CHCl_3$. Its yield depended greatly on the mole ratio of the reagents, reaching an almost quantitative ratio for a fourfold excess of TMDS (experiment 4). The products of the reaction of TMDS, just as during catalytic condensation, were linear polysiloxanes with n = 1-3. In all the experiments, predominantly trisiloxane (n = 1) was formed, with the ratios between the polysiloxanes not changing significantly; they practically did not differ from the ratios of the polysiloxanes during condensation of TMDS in the presence of PdCl₂. It can be assumed that the scheme of their formation is identical. However, the yield of dimethylsilane, which should be significant, was extremely low (see Table 1). It is possible that the resulting $(CH_3)_2SiH_2$ was consumed for reduction of ChH to chloroform. For verification, $(CH_3)_2SiH_2$ was specially bubbled through an ether solution of ChH in the presence of a catalyst for 20 h. Chloroform (45% yield) was found in the reaction products, as well as linear polysiloxanes with n = 1-3. Without the catalyst, the reaction did not proceed.

During reduction of ChH, oxygen-containing products should also be formed, the most probable of which are CO or CH_2O . However, these compounds were not found among the reaction products. It is possible that CH_2O was reduced further. Indeed, during simultaneous bubbling of gaseous $(CH_3)_2SiH_2$ and CH_2O through a solvent in the presence of PdCl₂ or H_2PtCl_6 , tetramethyldihydrodisiloxane was formed. A similar reaction of CH_2O with triethyl-silane has been described [6]. In this case, the only reaction product was hexaethyldi-siloxane.

EXPERIMENTAL

The gaseous products were analyzed with a Tsvet-102 chromatograph with a katharometer detector. The quantitative determination was carried out according to calibration graphs. To identify the products, TCEA [7] and linear polysiloxanes with n = 1-3 [8] were synthesized.

The reactions with the catalyst were carried out in a Chugaev-Tserevetinov device, into various elbows of which were placed an ether solution of TMDS or its mixture with ChH and a catalyst in an amount 2% of the weight of the siloxane. The device was connected to a reflux condenser and via it to a buret. The contents of both elbows were poured together, and an exothermic reaction was observed.

<u>Reaction of TMDS with ChH without a Catalyst.</u> A. During the reaction of 5.36 g TMDS and 6.62 g ChH (1:1) at 80°C, 5.4 g TCEA, 0.24 g CHCl₃, and linear polysiloxanes with n = 1 (1.62 g), n = 2 (0.54 g), and n = 3 (0.46 g) were formed. The initial compounds reacted completely.

B. A mixture of 13.4 g TMDS and 16.5 g ChH was heated to 70°C. In several minutes, when the turbulent course of the reaction subsided, it was heated on a boiling water bath for another hour. The separated mixture was transferred to a separating funnel and treated

with hot water (3 × 50 ml). The aqueous part was extracted with ether (3 × 50 ml). The ether extract was dried with Na_2SO_4 . The solvent was distilled off, and the residue was distilled. We obtained 12 g (80%) TCEA [7], bp 95-97°C (125 mm), $n_D^{2°}$ 1.4865.

<u>Reaction of TMDS with Chloral.</u> We placed 4.94 g TMDS and 2.65 g chloral in an ampoule, evacuated the vessel, sealed it, and left it to stand at ~20°C for 10 h. Then the ampoule was opened, and the liquid phase was analyzed for TCEA content. Traces of CCl_3CH_2OH were found. The reaction mixture was kept under vacuum at 100°C for 30 min. The residue, viscous and nonvolatile under these conditions, was hydrolyzed with 0.6 ml water. We found 0.80 g TCEA in the hydrolysate.

Condensation of TMDS in the Presence of PdCl₂. During condensation of 5.00 g TMDS in an ether solution in the presence of 0.20 g PdCl₂, 165 ml dimethylsilane with an H₂ impurity was isolated after 10 days. Traces of the initial siloxane and linear polysiloxanes with n = 1 and 2 were found in the liquid fraction. After distillation of the reaction mixture, two products were isolated: 2.64 g H(CH₃)₂SiOSi(CH₃)₂OSi(CH₃)₂H [8], bp 128°C (760 mm) np^{2°} 1.3820. Found: C 34.20; H 9.30; Si 39.58%. C₆H₂oSi₃O₂. Calculated: C 34.57; H 9.50; Si 40.00%, and 0.82 g H(CH₃)₂Si[OSi(CH₃)₂]₂OSi(CH₃)₂H [8], bp 61°C (15 mm), np^{2°} 1.3882. Found: C 33.40; H 9.02; Si 39.08%. C₈H₂oSi₄O₃. Calculated: C 34.00; H 9.20; Si 39.50%.

Catalytic Reaction of TMDS and ChH. The reaction of TMDS with ChH in the presence of $PdCl_2$ was carried out for ratios of 1:2, 1:1, 2:1, and 4:1. Data of an experiment carried out for a ratio of 2:1 are given below.

In the reaction (80°C) of 2.68 g TMDS and 1.65 g ChH in the presence of 0.03 g PdCl₂, we found 0.68 g TMDS, 0.58 g ChH, 0.78 g CHCl₃, and linear polysiloxanes $H(CH_3)_2Si[OSi-(CH_3)_2]_nOSi(CH_3)_2H$, 0.95 g (n = 1), 0.35 g (n = 2), and 0.06 g (n = 3), after 30 min in the liquid phase.

<u>Catalytic Reaction of Dimethylsilane and ChH.</u> Dimethylsilane was bubbled into a solution of 6.62 g ChH in 20 ml abs. ether and 0.20 g PdCl₂ and H_2PtCl_6 at ~20°C for 20 h at a rate of 20 ml/min. Then the ether was distilled off, and the residue was chromatographed. We found 3.00 g unreacted ChH, 1.95 g CHCl₃, and 0.75 g TCEA. We also found linear polysiloxanes with n = 1-3.

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CONCLUSIONS

Tetramethyldihydrodisiloxane reacts with chloral hydrate, giving trichloroethyl alcohol in a high yield; the reaction is convenient for preparative purposes. In the presence of PdCl₂ or H₂PtCl₆, the main product is chloroform.

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