REACTION OF (CHLOROMETHYL)CHLOROSILANES WITH tert-BUTYL ALCOHOL

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Previously it was shown that the reaction of tert-BuOH with (α-chloroethyl)trichlorosilane gives a polymer and tert-BuCl [1]. It seemed of interest to study the reaction of the (chloromethyl)chlorosilanes with tert-BuOH and follow the effect of replacing the CH_3 groups on the silicon. It proved that (chloromethyl)dimethylchlorosilane reacts with noticeable speed when heated to give tert-BuCl in 99.3% yield and 1,3-di(chloromethyl)tertramethyldisiloxane. The activity increases when the CH_3 group in the (chloromethyl)chlorosilanes is replaced by halogen. Thus, tert-BuCl is formed in 95.2% yield in the case of (chloromethyl)methyldichlorosilane, and also (chloromethyl)methylsiloxane oligomers, which represent a liquid with ν =219 cS.

$$n\mathrm{ClCH_2SiCl_2(CH_3)} + 2n(\mathrm{CH_3})_3\mathrm{COH} \rightarrow -\left(\begin{array}{c}\mathrm{CH_3}\\ |\\ -\mathrm{Si}-\\ |\\ \mathrm{CH_2Cl}\end{array}-\mathrm{O}-\right)_n- + 2n(\mathrm{CH_3})_3\mathrm{CCl} + n\mathrm{H_2O}$$

The IR spectrum and elemental analysis correspond to the indicated composition of the oligomer. When chloromethyl)trichlorosilane is mixed with tert-BuOH, the reaction proceeds by the following scheme:

$$n\ \mathrm{ClCH_2SiCl_3} + 3n\ (\mathrm{CH_3})_3\mathrm{COH} \rightarrow (\mathrm{ClCH_2SiO_{1.5}})_n + 3n(\mathrm{CH_3})_3\mathrm{CCl} + 1.5n\mathrm{H_2O}$$

Here are formed tert-BuCl in 90.6% yield and the polymer with the indicated composition. The latter is an insoluble and infusible product, whose thermogravimetric analysis curve is shown in Fig. 1.

EXPERIMENTAL METHOD

Reaction of (Chloromethyl)methyldichlorosilane with tert-Butanol. With stirring, 16.3 g (2.2 moles) of tert-BuOH was added in drops to 23.9 g (0.1 mole) of (chloromethyl)methyldichlorosilane. Here the temperature rose from 20 to 26°C. On conclusion of HCl evolution the reaction mixture was allowed to cool and then evacuated, collecting the low-boiling-point fraction in a trap. Distillation of this fraction gave 17.6 g (95.2%) of tert-BuCl, bp 49-50°, n_D^{20} 1.3860. The residue was 12.2 g (96.4%) of poly(chloromethyl)methylsiloxane. Infrared spectrum (ν, cm^{-1}): 1060-1120 (Si–O–Si); 820, 1270 (Si–Me); 660 C–Cl [2]. Found: C 22.13; H 4.65; Si 25.80; Cl 31.88%. $(C_5H_5ClOSi)_n$. Calculated: C 22.12; H 4.65; Si 25.95; Cl 32.64%.

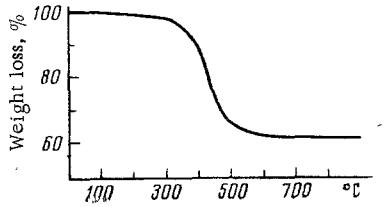

Fig. 1. Thermograviogram of polymer obtained by the reaction of (chloromethyl)trichlorosilane with tert-BuOH.

Reaction of Chloromethyl)trichlorosilane with tert-Butanol. The reaction was carried out in a similar manner. To 18.4 g (0.1 mole) of (chloromethyl)trichlorosilane was added 24.4 g (0.33 mole) of tert-BuOH in drops. The maximum temperature during mixing was 45°. We obtained 25.2 g (90.6%) of tert-BuCl and 8.8 g (87.1%) of a polymer. Found: C 11.92; H 1.97; Cl 34.97; Si 27.58%. $(ClCH_2SiO_{1.5})_n$. Calculated: C 13.44; H 2.77; Cl 31.71; Si 27.01%.

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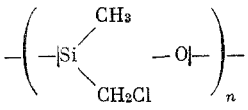
CONCLUSIONS

The reaction of tert-butanol with (chloromethyl) methyldichlorosilane and (chloromethyl)trichlorosilane leads to the formation of tert-butyl chloride and, respectively, polymers with the composition

 and $(ClCH_2SiO_{1.5})_n$.

LITERATURE CITED

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2. L. J. Bellamy, Infrared Spectra of Complex Molecules, Wiley (1958).