REACTION OF 1,5-DIHYDROORGANOTRISILOXANES WITH ORGANOSILANOLS

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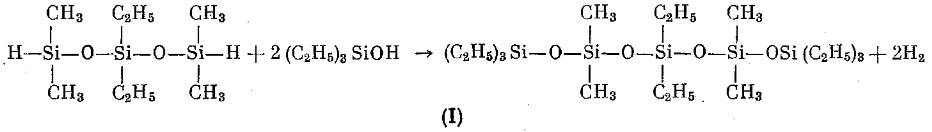
UDC 542.91+546.287

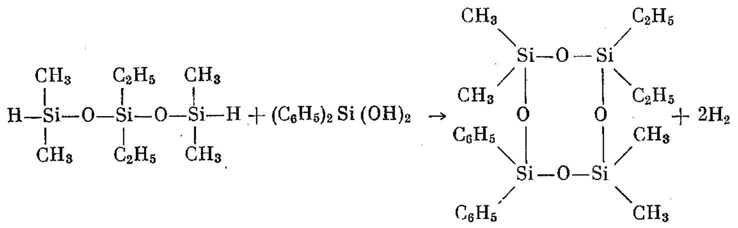
A method has been put forward for the production of organosiloxanes by catalytic condensation of hydroorganosilanes and organosilanols with organosilanols in the presence of colloidal nickel [1], H_2PtCl_6 and anhydrous $ZnCl_2$ [2]. The authors of [2] showed that with increase in size of the siloxane chains the reactivity of the dihydrosiloxanes was reduced and the condensation was limited.

We have achieved the condensation of 1,5-dihydroorganotrisiloxanes with organosilanols with catalytic quantities of KOH, in the following manner



$$\mathrm{H{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{C_2H_5}{\overset{C_2H_5}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}H + 2\,(C_2H_5)_3SiOH \rightarrow (C_2H_5)_3Si{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{C_2H_5}{\overset{C_2H_5}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}OSi(C_2H_5)_3 + 2H_2}$$

(I)



(II)

EXPERIMENTAL

The quantity of hydrogen evolved corresponded to the equation. The hydrogen was identified chromatographically. The compounds obtained (yields up to 80%) had the following characteristics. Compound (I): bp 156-157° (2.5 mm); n_D^{20} 1.4270; d_4^{20} 0.8991. Found %: C 47.79, 47.60; H 10.26, 10.24; Si 28.72, 28.89. MR 141.90; mol. wt. 486.5. $Si_5C_{20}H_{32}O_4$. Calculated %: C 48.32; H 10.54; Si 28.25. MR 140.92; mol. wt. 497.06.

Compound (II), bp 160° (4.5 mm); n_D^{20} 1.4900; d_4^{20} 1.0445. Found %: C 53.27, 53.43; H 6.89, 6.93; Si 24.75, 24.93. MR 124.19; mol. wt. 434.0. $Si_4C_{20}H_{32}O_4$. Calculated %: C 53.52; H 7.18; Si 25.03. MR 123.22; mol. wt. 448.8.

The reactions proceed slowly at room temperature but rapidly at 65-100°. The catalyst indicated is very active. The reactions may be carried out either in solution (dioxane), or without solvent.

This reaction leads to the synthesis of organocyclosiloxanes with different diorganosiloxane groups in known positions in the ring. By the reaction of dihydroorganotrisiloxanes with organosilanols there is no noticeable evolution of dimethylsilane as is the case when catalytic quantities of KOH act on α,ω-dihydroorganosiloxanes [3] and on tetramethylcyclotetrasiloxane [4].

CONCLUSIONS

1. The condensation of 1,5-dihydroorganotrisiloxanes with organosilanols using catalytic quantities of KOH has been studied.

M. V. Lomonosov Moscow Institute of Fine chemical Technology; Tbilisi State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2146-2147, September, 1968. Original article submitted March 15, 1968.

2. Using diorganosilanediols this reaction leads to the synthesis of organocyclosiloxanes with diorganosiloxane groups in known positions in the ring.

LITERATURE CITED

1. N. F. Orlov and V. N. Dolgov, DAN SSSR, 125, 817 (1959).
2. S. N. Borisov, N. G. Sviridova, and V. S. Orlova, ZhOKh, 36, 687 (1966).
3. K. A. Andrianov, L. M. Khananashvili, V. M. Kopylov, and T. V. Nesterova, Vysokomolekul. soed., 9, B-6, 413 (1967).
4. G. L. Lee, J. Organometal. Chem., 6, 603 (1966).