BICYCLIC DIMETHYLSILOXANE OLIGOMERS*

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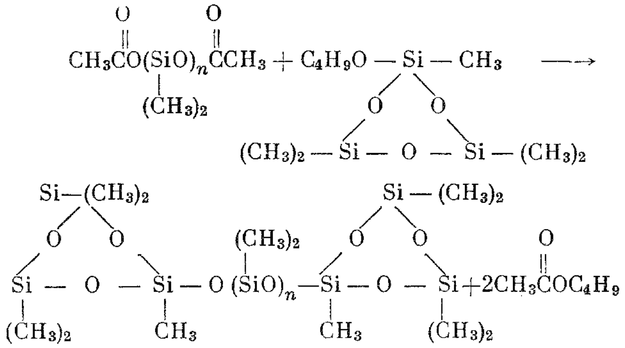
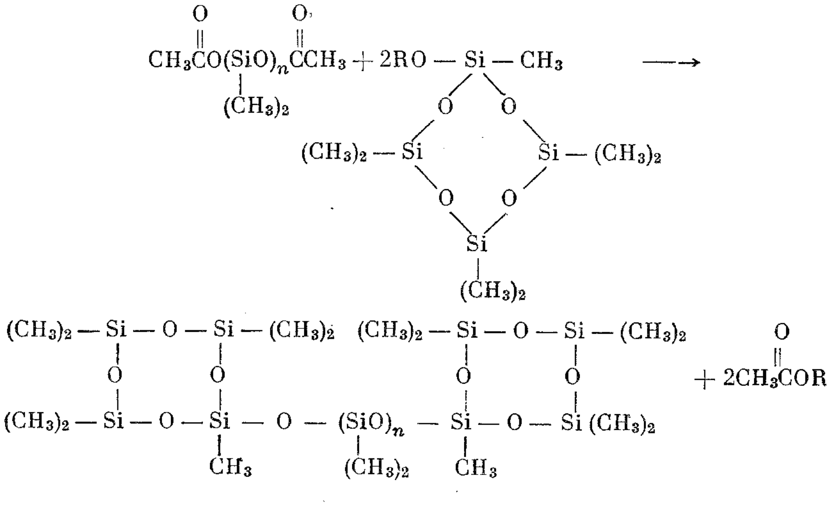
The synthesis of polymers of regular reticular structure on the basis of the decyclization of inorganic rings is bound up with the development of methods for the preparation of bicyclic oligomers. In the present investigation we studied the heterofunctional condensation between α,ω-diacetoxypoly(dimethylsiloxanes) [or α,ω-diacetoxypoly(methylphenylsiloxanes)] and alkoxymethylcyclosiloxanes. The experiments showed that in the condensation of 1,3-diacetoxytetramethyldisiloxane, 1,5-diacetoxyhexamethyltrisiloxane, and 1,7-diacetoxyoctamethyltetrasiloxane with butoxypentamethylcyclotrisiloxane, dimethylsiloxanes are formed which contain six-membered dimethylsiloxane rings at the ends of the molecules:



in which n = 2, 3, 4.

By the condensation of 1,3-diacetoxytetramethyldisiloxane, 1,5-diacetoxyhexamethyltrisiloxane, 1,7-diacetoxyoctamethyltetrasiloxane, and 1,9-diacetoxydecamethylpentasiloxane with butoxyheptamethylcyclotetrasiloxane and with ethoxyheptamethylcyclotetrasiloxane we obtained bicyclic compounds containing eight-membered dimethylsiloxane rings at the ends of the molecules:



where n = 2, 3, 4, 5, R = C_2H_5, C_4H_9.

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An oligomer containing silicon-attached methyl and phenyl groups in the linear chain of the molecule, namely 1,3-bis(heptamethylcyclotetrasiloxanoxy)-1,3-dimethyl-1,3-diphenyldisiloxane, was prepared by the heterofunctional condensation of 1,3-diacetoxy-1,3-dimethyl-1,3-diphenyldisiloxane with butoxyheptamethylcyclotetrasiloxane. In the course of the condensation 95.2-98% of butyl acetate (ethyl acetate) is formed, in agreement with the above equations for the reactions.

All the bicyclic oligomers isolated are clear colorless liquids, which can be distilled without decomposition and are readily soluble in ether, ethyl acetate, butyl acetate, benzene, toluene, and ethanol. The structures of the compounds obtained were determined from their elementary composition and molecular weights. In confirmation of the structures of the bicyclic compounds obtained it was established that functional groups (OH and alkoxy) are absent, and the presence of rings was confirmed by the catalytic polymerization of these compounds. Under the action of catalytic amounts of alkali the bicyclic dimethylsiloxanes were converted into insoluble polymers even at room temperature. This confirms not only the presence of rings, but also the presence of a silicon atom attached to three oxygen atoms. It is known that dimethylsiloxane rings polymerize in presence of alkalies only at temperatures above 100°, but dimethylsiloxane rings containing a silicon atom that is attached to three oxygen atoms polymerize at room temperature. The α,ω-diacetoxydimethylsiloxanes used in this work were synthesized by the condensation of α,ω-dichlorodimethylsiloxanes with acetic anhydride.

EXPERIMENTAL

Ethoxy- and butoxy-heptamethylcyclotetrasiloxanes were synthesized by the method that we proposed earlier [1]. The procedure in the heterofunctional condensation was that proposed by Andrianov and Dabagova [2].

1,3-Diacetoxytetramethyldisiloxane. A mixture of 28.1 g of 1,3-dichlorotetramethyldisiloxane and 24 g of acetic anhydride was heated at 140° for 5 h. Acetyl chloride was distilled off (14 g). Vacuum distillation gave excess of acetic anhydride and 1,3-diacetoxytetramethyldisiloxane, b.p. 65° (2 mm) in 82% yield; $n^{20}D$ 1.4022, d^{20}_4 1.0250. Found: Si 21.87; C 38.6; H 7.3; CH_3COO^- 46.9%; MR 59.24. $C_8H_{18}Si_2O_5$. Calculated: Si 22.4; C 38.4; H 7.2; CH_3COO^- 47.2%; MR 59.65.

1,5-Diacetoxyhexamethyltrisiloxane. The procedure was as for 1,3-diacetoxytetramethyldisiloxane. We obtained 1,5-diacetoxyhexamethyltrisiloxane, b.p. 92.5° (2 mm) in 86% yield; $n^{20}D$ 1.4029; d^{20}_4 1.0118. Found: Si 25.21; C 36.93; H 7.5; CH_3COO^- 36.1%; MR 77.71. $C_{10}H_{24}Si_3O_6$. Calculated: Si 25.9; C 37.0; H 7.4; CH_3COO^- 36.4%.

1,7-Diacetoxyoctamethyltetrasiloxane. The procedure was as for 1,3-diacetoxytetramethyldisiloxane. We obtained 1,7-diacetoxyoctamethyltetrasiloxane, b.p. 108° (2 mm), in 84% yield; $n^{20}D$ 1.4029; d^{20}_4 1.0081. Found: Si 28.4; C 35.8; H 7.64; CH_3COO^- 29.3%; MR 97.15. $C_{12}H_{30}Si_4O_7$. Calculated: Si 28.15; C 36.1; H 7.5; CH_3COO^- 29.6%; MR 96.5.

1,9-Diacetoxydecamethylpentasiloxane. The procedure was as for 1,3-diacetoxytetramethyldisiloxane. We obtained 1,9-diacetoxydecamethylpentasiloxane, b.p. 134° (2 mm) in 85% yield; $n^{20}D$ 1.4038; d^{20}_4 1.0021. Found: Si 29.55; C 35.53; H 7.7; CH_3COO^- 24.4%; MR 115.84. $C_{14}H_{36}Si_5O_8$. Calculated: Si 29.7; C 35.53; H 7.6; CH_3COO^- 24.7%.

1,3-Bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane. A mixture of 4.2 g of 1,3-diacetoxytetramethyldisiloxane, 9.7 g of butoxypentamethylcyclotrisiloxane, and 1.2 ml of 36% hydrochloric acid was stirred for 1 h. The reaction mixture was diluted with 15 ml of ether and washed with water until neutral. Ether and 3.4 g of butyl acetate were distilled off. The residue was vacuum-fractionated from a quartz flask, and as a result of three fractionations we isolated 2.2 g (22%) of 1,3-bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane; b.p. 126.5° (2 mm); $n^{20}D$ 1.4053; d^{20}_4 1.020. Found: Si 38.28, 37.98; C 29.44, 29.51; H 7.5, 7.6%; mol. wt. 578.1; MR 139.3. $C_{14}H_{42}Si_8O_9$. Calculated: Si 38.79; C 29.04; H 7.3%; mol. wt. 579.2; MR 138.0.

1,5-Bis(pentamethylcyclotrisiloxanoxy)hexamethyltrisiloxane. Analogously, from 16.9 g of 1,5-diacetoxyhexamethyltrisiloxane and 32.1 g of butoxypentamethylcyclotrisiloxane we obtained 6.1 g (17.8%) of 1,5-bis(pentamethylcyclotrisiloxanoxy)hexamethyltrisiloxane; b.p. 144-146° (1.5 mm); $n^{20}D$ 1.4055; d^{20}_4 1.022. Found: Si 38.21; C 29.94; H 6.2%; mol. wt. 651.4; MR 156.73. $C_{16}H_{48}Si_9O_{10}$. Calculated: Si 38.69; C 29.4; H 5.98%; mol. wt. 653.4; MR 156.76.

1,7-Bis(pentamethylcyclotrisiloxanoxy)octamethyltetrasiloxane. The procedure was as for 1,3-bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane. From 7.3 g of 1,7-diacetoxyoctamethyltetrasiloxane and 11.1 g of butoxypentamethylcyclotrisiloxane we obtained 2.6 g of 1,7-bis(pentamethylcyclotrisiloxanoxy)octamethyltetrasiloxane; b.p. 161-164° (1.5 mm); yield 18.3%; $n^{20}D$ 1.4058; d^{20}_4 1.025. Found: Si 38.4; C 29.4; H 7.4%; mol. wt. 725.2; MR 174.29. $C_{18}H_{54}Si_{10}O_{11}$. Calculated: Si 38.6; C 29.04; H 7.3%; mol. wt. 727.5; MR 175.4.

1,3-Bis(heptamethylcyclotetrasiloxanoxy)tetramethyldisiloxane. By a procedure analogous to that for the preparation of 1,3-bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane, from 5.05 g of 1,3-diacetoxytetramethyldisiloxane and 15.7 g of butoxyheptamethylcyclotetrasiloxane we obtained 3.7 g (32%) of 1,3-bis(heptamethylcyclotetrasiloxanoxy)tetramethyldisiloxane; b.p. 158-161° (2 mm); $n^{20}D$ 1.4060; d^{20}_4 1.0260. Found: Si 38.16; C 29.61; H 7.8%; mol. wt. 801.07; MR 192.40. $C_{20}H_{60}Si_{11}O_{12}$. Calculated: Si 38.54; C 29.96; H 7.54%; mol. wt. 801.67; MR 194.20.

1,7-Bis(heptamethylcyclotetrasiloxanoxy)octamethyltetrasiloxane. By a procedure analogous to that for the preparation of 1,3-bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane, from 7.9 g of 1,7-diacetoxyoctamethyltetrasiloxane and 15 g of butoxyheptamethylcyclotetrasiloxane we obtained 6 g (29.8%) of 1,7-bis(heptamethylcyclotetrasiloxanoxy)octamethyltetrasiloxane; b.p. 196-199° (1.5 mm); $n^{20}D$ 1.4076; d^{20}_4 1.0260. Found: Si 29.77; C 38.9; H 7.7%; mol. wt. 872.3; MR 210.8. $C_{22}H_{66}Si_{12}O_{13}$. Calculated: Si 30.16; C 38.48; H 7.5; mol. wt. 875.8; MR 212.9.

1,9-Bis(heptamethylcyclotetrasiloxanoxy)decamethylpentasiloxane. By a procedure analogous to that for the preparation of 1,3-bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane, from 5.1 g of 1,9-diacetoxydecamethylpentasiloxane and 7.6 g of butoxyheptamethylcyclotetrasiloxane we obtained 2.6 g of 1,9-bis(heptamethylcyclotetrasiloxanoxy)decamethylpentasiloxane; b.p. 218-220° (1.5 mm); $n^{20}D$ 1.4081; d^{20}_4 1.0266. Found: Si 37.98; C 30.47; H 7.7%; mol. wt. 946.2; MR 230.55. $C_{24}H_{72}Si_{13}O_{14}$. Calculated: Si 38.4; C 30.3; H 7.6%; mol. wt. 949.6; MR 228.17.

1,3-Bis(heptamethylcyclotetrasiloxanoxy)-1,3-dimethyl-1,3-diphenyldisiloxane. By the above-described procedure, from 3.6 g of 1,3-diacetoxy-1,3-dimethyl-1,3-diphenyldisiloxane we prepared 2.2 g (24%) of 1,3-bis(heptamethylcyclotetrasiloxanoxy)-1,3-dimethyl-1,3-diphenyldisiloxane; b.p. 302° (1.5 mm); $n^{20}D$ 1.4022; d^{20}_4 1.0547. Found: Si 39.72; C 39.71; H 6.9%; mol. wt. 847.1. $C_{28}H_{58}Si_{10}O_{11}$. Calculated: Si 32.97; C 39.46; H 6.8%; mol. wt. 851.56.

SUMMARY

1. By the heterofunctional condensation of 1,3-diacetoxytetramethyldisiloxane, 1,5-diacetoxyhexamethyltrisiloxane, and 1,7-diacetoxyoctamethyltetrasiloxane with butoxypentamethylcyclotrisiloxane, of 1,3-diacetoxytetramethyldisiloxane, 1,5-diacetoxyhexamethyltrisiloxane, 1,7-diacetoxyoctamethyltetrasiloxane, and 1,9-diacetoxydecamethylpentasiloxane with butoxyheptamethylcyclotetrasiloxane, and of 1,3-diacetoxy-1,3-dimethyl-1,3-diphenyldisiloxane with butoxyheptamethylcyclotetrasiloxane we synthesized: 1,3-bis(pentamethylcyclotrisiloxanoxy)tetramethyldisiloxane; 1,5-bis(pentamethylcyclotrisiloxanoxy)hexamethyltrisiloxane; 1,7-bis(pentamethylcyclotrisiloxanoxy)octamethyltetrasiloxane; 1,3-bis(heptamethylcyclotetrasiloxanoxy)tetramethyldisiloxane; 1,5-bis(heptamethylcyclotetrasiloxanoxy)hexamethyltrisiloxane; 1,7-bis(heptamethylcyclotetrasiloxanoxy)octamethyltetrasiloxane; 1,9-bis(heptamethylcyclotetrasiloxanoxy)decamethylpentasiloxane; and 1,3-bis(heptamethylcyclotetrasiloxanoxy)-1,3-dimethyl-1,3-diphenyldisiloxane.

2. By the acetylation of 1,3-dichlorotetramethyldisiloxane, 1,5-dichlorohexamethyltrisiloxane, 1,7-dichlorooctamethyltetrasiloxane, and 1,9-dichlorodecamethylpentasiloxane with acetic anhydride we obtained 1,3-diacetoxytetramethyldisiloxane, 1,5-diacetoxyhexamethyltrisiloxane, 1,7-diacetoxyoctamethyltetrasiloxane, and 1,9-diacetoxydecamethylpentasiloxane.

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