SYNTHESIS OF METHYLPHENYL(DIETHYL)CYCLOMETHYLPHOSPHONOXYSILOXANES

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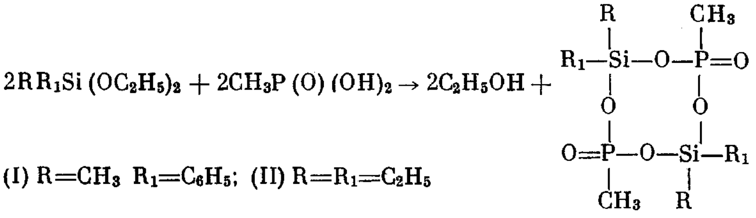
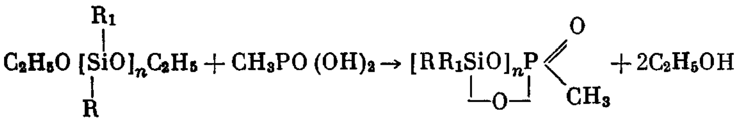
In a previous paper it was shown by us that the condensation of methylphosphonic acid with dimethyldiethoxysilane and α,ω-diethoxydimethylsiloxanes does not lead to the synthesis of linear polymers, and, instead, cyclic products are formed predominantly [1]. It was interesting to follow the influence of the groups attached to silicon on the condensation of diethoxyorganosiloxanes with methylphosphonic acid. In this paper we studied the condensation of methylphosphonic acid with phenylmethyldiethoxysilane, diethyldiethoxysilane, α,ω-diethoxymethylphenylsiloxanes, and α,ω-diethoxydiethylsiloxanes. A study of the reaction revealed that methylphosphonic acid reacts easily with methylphenyldiethoxysilane; as a result, alcohol is liberated and low-molecular, distillable products are formed in up to 95% yield, from which the cyclic compound was isolated (70% yield)



$$2RR_1Si(OC_2H_5)_2 + 2CH_3P(O)(OH)_2 \rightarrow 2C_2H_5OH +$$

(I) $R=CH_3$ $R_1=C_6H_5$; (II) $R=R_1=C_2H_5$

Similar results were obtained when diethyldiethoxysilane was condensed with methylphosphonic acid. It should be mentioned that Orlov and Voronkov obtained only the polymer when they reacted methylphosphonic acid with diethyldiethoxysilane [2]. If the condensation is run with α,ω-diethoxymethylphenylsiloxanes, where the ethoxyl groups are separated by two, three or four methylphenylsiloxane groups, then in this case cyclic compounds are formed predominantly. The reaction goes according to the scheme



$$C_2H_5O[\overset{R_1}{\underset{R}{Si}}O]_nC_2H_5 + CH_3PO(OH)_2 \rightarrow [RR_1SiO]_nP(=O)(CH_3) + 2C_2H_5OH$$

(I) $R=CH_3$ $R_1=C_6H_5$ $n=2, 3, 4$; (II) $R=R_1=C_2H_5$ $n=2, 3$.

The formed cyclic compounds contain exactly the same number of methylphenylsiloxane units as were present in the taken α,ω-diethoxymethylphenylsiloxane. The use of α,ω-diethoxydiethylsiloxanes in this reaction leads to the same results. This interesting and peculiar course for the reaction under relatively mild conditions, leading to the formation of cyclic low molecular compounds, and not of polymers, is probably associated with the greater flexibility of the siloxane and phosphoryloxane chains. The isolated compounds are either viscous liquids (diethylcyclomethylphosphonoxysiloxanes) or waxy substances (methylphenylcyclomethylphosphonoxysiloxanes) that are readily distillable in vacuo. They are readily soluble in aromatic hydrocarbons and are easily hydrolyzed by water. The physicochemical properties are given in Tables 1 and 2. Chemical analysis and molecular weight determination disclosed that the isolated compounds have a cyclic structure.

TABLE 1. Methylphenylcyclomethylphosphonoxysiloxanes

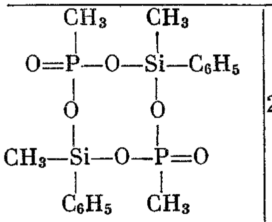
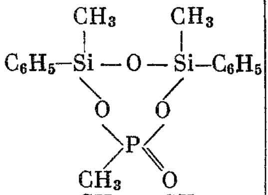
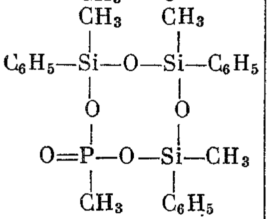
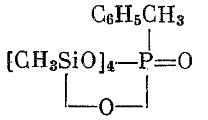
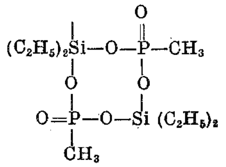
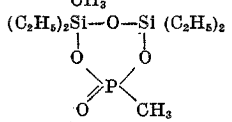
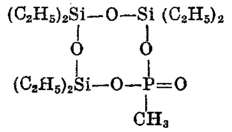
Compound	B.p., °C (p, mm of Hg)	Found					Calculated				
		C,%	H,%	P, %	Si, %	mol. wt.	C,%	H,%	P,%	Si,%	mol. wt.
	252—255 (2)	45,27	5,50	14,67	13,36	430,9	44,84	5,17	14,43	13,10	428,5
	242—244 (2)	51,08	5,89	8,17	14,85	354,5	51,41	5,46	8,84	16,03	350,5
	267—268 (2)	54,1	5,90	5,85	16,73	—	54,3	5,55	6,37	17,32	—
	275—276 (1)	55,0	5,85	4,65	16,75	632,4	55,86	5,66	4,98	18,0	622,9

TABLE 2. Diethylcyclomethylphosphonoxysiloxanes

Compound	B.p., °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found					Calculated				
				MR	C, %	H, %	P, %	Si,%	*MR*	C, %	H, %	P, %	Si, %
	226—229 (5)	1,4540	1,174	88,10	33,39	7,52	15,9	15,26	88,43	33, 32	7,27	17,19	15,59
	168—170 (2)	1,4490	1,091	69,44	37,74	8,28	10,43	19,00	69,62	38,28	8,21	10,97	19,90
	163—165 (1)	1,4450	1.069	95,76	40,64	8,72	7,60	21,16	95,52	40,59	8,64	8,05	21,92

To confirm the structure of 1,3,5,7-tetramethyl-1,5-diphenylcyclo-3,7-phosphonoxydisiloxane we took its infrared spectrum: the presence of absorption bands in the 930-1100, 1320, 1430, 1280 and 1265 cm^{-1} regions testifies that the Si—O—P, P=O, P—CH_3, Si—C_6H_5 and Si—CH_3 bonds are present. To confirm the cyclic structure of 1,3,5-trimethyl-3,5-diphenylcyclo-1-phosphonoxydisiloxane we took the NMR spectrum of this compound and of the starting α,ω-diethoxymethylphenylsiloxane, both shown in Fig. 1. Four types of protons were detected for 1,3-diethoxy-1,3-dimethyl-1,3-diphenyldisiloxane: CH_3 in the Si—CH_3 group, C_6H_5 in the Si—C_6H_5 group, and CH_3 and

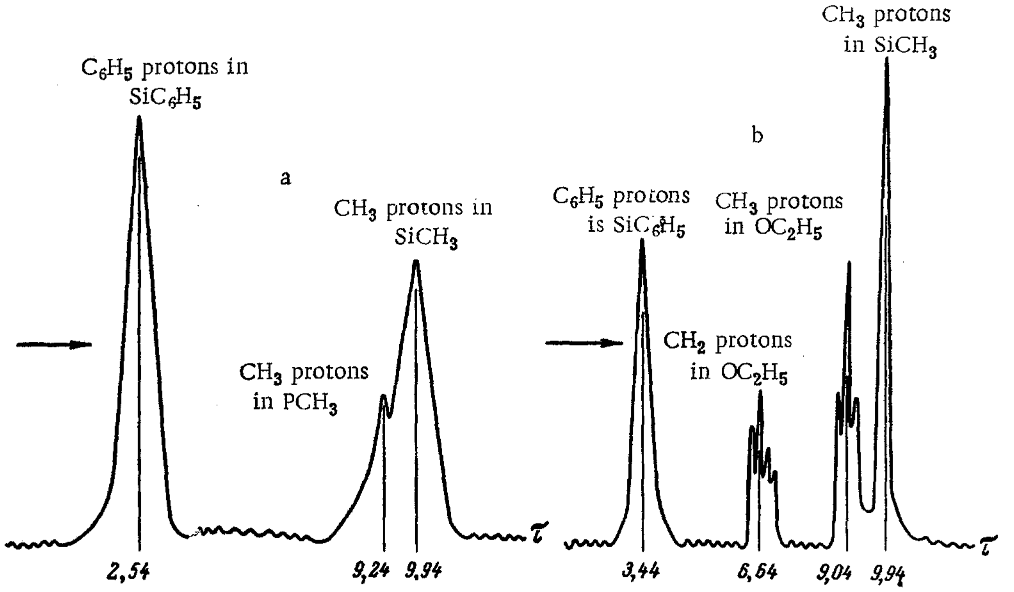


Fig. 1. NMR spectra: a) 1,3,5-trimethyl-3,5-diphenylcyclo-1-phosphonoxydisiloxane; b) 1,3-diethoxy-1,3-dimethyl-1,3-diphenyldisiloxane.

TABLE 3. α,ω-Diethoxysiloxanes

Compound	B. p., °C (p, mm of Hg)	n_D^{20}	d_4^{20}	*MR*		OC_2H_5	
				found	calcd.	found	calcd.
$C_2H_5O\,[CH_3C_6H_5SiO]_2C_2H_5$	175—176 (4)	1,5012	1,028	90,34	90,33	26,02	25,59
$C_2H_5O\,[CH_3C_6H_5SiO]_3C_2H_5$	246—247 (2)	1,5130	1,051	138,10	137,85	19,06	18,66
$C_2H_5O\,[CH_3C_6H_5SiO]_4C_2H_5$	269—270 (2)	1,5253	1,076	176,20	176,26	14,33	14,55
$C_2H_5O\,[(C_2H_5)_2SiO]_2C_2H_5$	225—230	1,4152	0,8976	77,75	78,41	32,09	32,35
$C_2H_5O\,[(C_2H_5)_2SiO]_3C_2H_5$	90—92 (2)	1,4215	0,9166	105,4	106,12	24,03	23,67

CH_2 in the OC_2H_5 group. The following protons were detected for 1,3,5-trimethyl-3,5-diphenylcyclo-1-phosphonoxydisiloxane: CH_3 in the $Si-CH_3$ group, C_6H_5 in the $Si-C_6H_5$ group, and CH_3 in the $P-CH_3$ group. The absence of other protons indicates the absence of terminal groups and is proof of the cyclic structure of the compound.

EXPERIMENTAL

The diethoxydiethyl(methylphenyl)silanes were obtained by the etherification of the diethyl(methylphenyl)-dichlorosilanes, using ammonia as the HCl acceptor. The α,ω-diethoxydiethylsiloxanes and α,ω-diethoxymethylphenylsiloxanes were obtained by the partial hydrolysis of the diethoxydiethyl(methylphenyl)silanes. The hydrolysis was run with 50% aqueous alcohol solution, and the amount of water was calculated using the equation $A = N/(N-N_1)$ where A is the average degree of polymerization of the obtained product, N is the number of moles of the starting monomer, and N_1 is the number of moles of water. After distilling off the alcohol and fractional distillation of the reaction products in vacuo we obtained the α,ω-diethoxysiloxanes, the properties of which are given in Table 3.

The constants of the first three compounds are somewhat different from those given in the literature [3], which obviously is due to the presence of isomers. The diethoxydiethylsiloxanes described in the literature contain 4, 7, 8 and 10 silicon atoms [4]; we were the first to isolate and characterize 1,3-diethoxy-1,1,3,3-tetraethyldisoloxane and 1,5-diethoxy-1,1,3,3,5,5-hexaethyltrisiloxane. The elemental analysis data and the molecular weight determination confirmed the composition of the diethoxysiloxanes.

All of the cyclic silicon organophosphorus compounds were synthesized by the same method: into a Wurtz flask, fitted with a magnetic stirrer, were charged the calculated amounts of reactants; after distilling off the alcohol (90-95% of theory, temperature of reaction mass 130-140°) the reaction products were fractionally distilled in vacuo. The still residue did not exceed 6-9%. The yield of cyclic compounds was 60-70%.

SUMMARY

1. 1,3-Diethoxy-1,1,3,3-tetraethyldisiloxane and 1,5-diethoxy-1,1,3,3,5,5-hexaethyltrisiloxane were isolated and characterized.

2. The condensation of α,ω-diethoxymethylphenylsiloxanes and α,ω-diethoxydiethylsiloxanes with methylphosphonic acid was studied. We isolateo and characterized seven members of the class of organocyclomethylphosphonoxysiloxanes.

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