TABLE 4. Kinetic Constants of the Interaction of S-β-Benzylmercaptoethyl Esters of Phosphorus Thioacids $RR^1P(O)SCH_2CH_2SCH_2Ph$ with Cholinesterases

Compound	R	R¹	AChE			BuChE		
			k_a, liter/mole·min	$K_{i,r}$, moles/liter	$K_{i,s}$, moles/liter	k_a, liter/mole·min	$K_{i,r}$, moles/liter	$K_{i,s}$, moles/liter
(I)	Me	EtO	$2{,}5\cdot10^7$	–*	–	$5{,}8\cdot10^5$	–	–
(II)	Me	BuO	$2{,}5\cdot10^7$	$2{,}2\cdot10^{-9}$	$4{,}1\cdot10^{-9}$	$5{,}3\cdot10^7$	$2{,}8\cdot10^{-9}$	$7{,}3\cdot10^{-10}$
(III)	Me	$C_6H_{11}O$	$8{,}3\cdot10^5$	$2{,}4\cdot10^{-6}$	$8{,}4\cdot10^{-7}$	$3{,}8\cdot10^6$	$4{,}0\cdot10^{-8}$	$6{,}7\cdot10^{-8}$
(IV)	Ph	EtO	$6{,}7\cdot10^4$	$1{,}6\cdot10^{-6}$	$4{,}6\cdot10^{-7}$	$1{,}4\cdot10^6$	$6{,}6\cdot10^{-8}$	$1{,}1\cdot10^{-7}$
(V)	C_6H_{11}	EtO	$1{,}8\cdot10^2$	$5{,}5\cdot10^{-4}$	$2{,}0\cdot10^{-5}$	$5{,}6\cdot10^4$	$1{,}7\cdot10^{-6}$	$4{,}2\cdot10^{-6}$
(VI)	EtO	EtO	$1{,}6\cdot10^4$	–	–	$1{,}7\cdot10^6$	–	–
(VII)	BuO	BuO	$2{,}5\cdot10^5$	$7{,}5\cdot10^{-7}$	$4{,}5\cdot10^{-7}$	$2{,}4\cdot10^7$	$6{,}5\cdot10^{-8}$	$2{,}0\cdot10^{-9}$
(VIII)	$C_6H_{13}O$	$C_6H_{13}O$	$4{,}3\cdot10^4$	$1{,}7\cdot10^{-6}$	$2{,}2\cdot10^{-7}$	$5{,}9\cdot10^6$	$2{,}6\cdot10^{-8}$	$3{,}8\cdot10^{-9}$

*Reversible components of inhibition could not be determined with sufficient reliability.

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SYNTHESIS AND PMR SPECTRA OF FUNCTIONAL METHYLCYCLOHEXA(HEPTA, OCTA)SILOXANES AND THEIR STRUCTURAL ISOMERS

N. N. Makarova and B. D. Lavrukhin

UDC 542.91:543.422.25:547.1'128

We have earlier reported the synthesis of functional methylcyclotetra(penta-, and hexa)-siloxanes, by the stepwise condensation of methyltrichlorosilane with dimethylsilanediol, 1,3-dihydroxytetramethyldisiloxane, and 1,5-dihydroxyhexamethyltrisiloxane [1]. The reaction between 1,1,7,7-tetrachlorohexamethyltetrasiloxane and 1,3-dihydroxytetramethyldisiloxane (DHMS) has given 2,8-dichloro-2,4,4,6,6,8,10,10,12,12-decamethylcyclohexasiloxane. In contrast, reaction of 1,1,5,5-tetrachlorotetramethyltrisiloxane with 1,5-dihydroxyhexamethyltrisiloxane (DHMTS) is more complex. It appears that intramolecular cyclization takes place by two routes to give both 2,6-dichloro-2,4,4,6,6,8,8,10,10,12,12-decamethylcyclohexasiloxane and its structural isomer.

We here continue a study of the condensation of α,α,ω,ω-tetrachlorodimethylsiloxanes with DHMTS with a view to obtaining 2,6-dichlorooctamethylcyclohexa- and 2,10-dichlorotetradecamethylcyclooctasiloxanes.

The reaction products were found by PMR to consist of a complex mixture of products, a common feature of which was the possession of $MeSiCl_2$ groups ($\delta Me \approx 0.8$ ppm) and MeSiCl ($\delta Me \approx 0.4$ ppm) groups. In addition, the elemental analyses of the fractions presumed to

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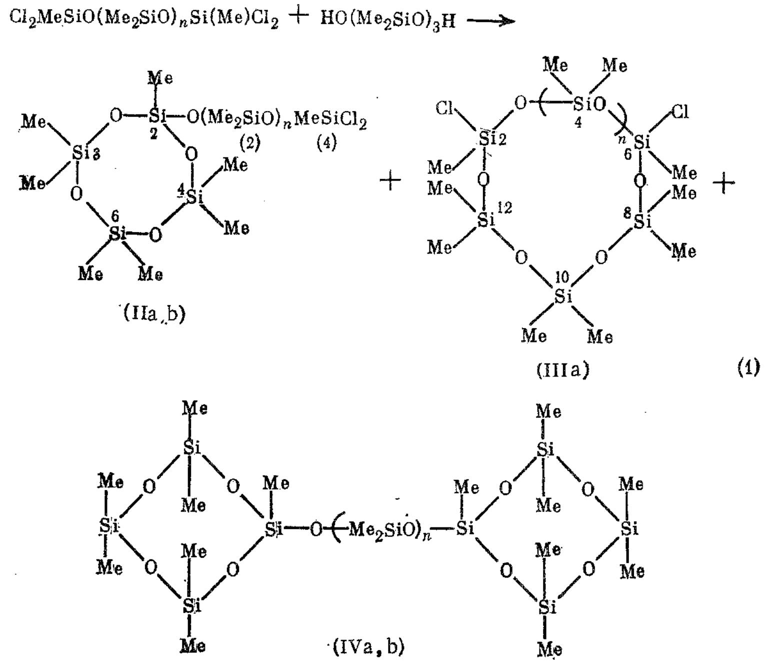
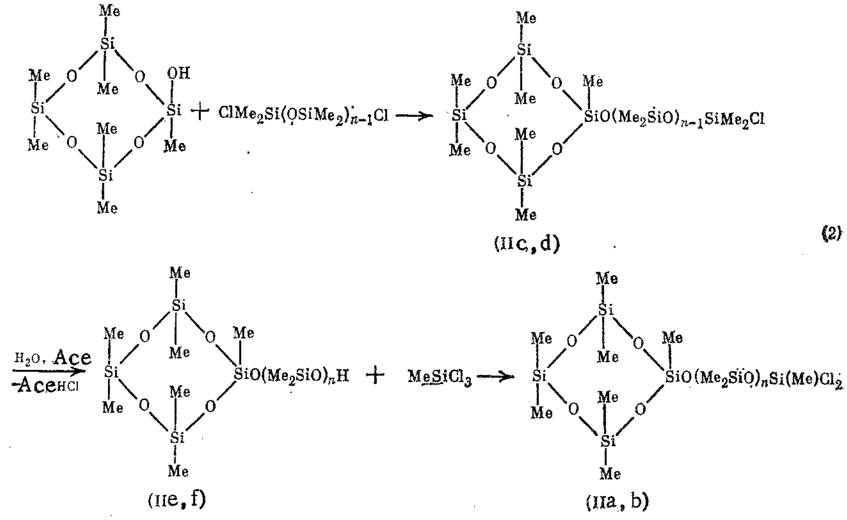
contain 2,6-dichlorodecamethylcyclooctasiloxane and 2,10-dichlorotetradecamethylcyclooctasiloxane were in agreement with the calculated values. In the mass spectra of the fractions of the products of the reaction between 1,1,5,5-tetrachlorotetramethyltrisiloxane and 1,1,9,9-tetrachlorooctamethylpentasiloxane with DHMTS, the peaks of greatest mass were those with m/z 469 and 617 respectively, corresponding to the loss of a methyl group from the molecular ions of dichloromethylcyclohexa-(and octa-)siloxanes or their structural isomers.

The PMR spectral data suggests that the condensation of α,α,ω,ω-tetrachlorodimethylsiloxanes with DHMTS involves intramolecular cyclization by two routes, as follows:



where $n = 1$ (a), 3 (b).

In order to confirm the formation of compounds with the proposed structure (II), it was attempted to obtain these compounds by direct synthesis (route 2)



$n = 1$ (c, e), 3 (d, f).

The physicochemical constants of the compounds (II) are shown in Table 1.

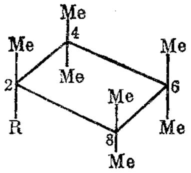
In the IR spectra of (IIa-f) (Table 1), in the region characteristic of ν_{as} vibrations of the Si–O bond, only (IIc) showed broadening of the absorption at 1080-1090 cm^{-1}, whereas in the other compounds (IIa, b, d-f) the band was split to form two maxima at 1040-1050 and 1050 cm^{-1}, it being observed that as the number of Me_2SiO units in the straight chain increased there was an increase in the intensity of the absorption at 1090 cm^{-1}. The IR spectra of (IIa-f) also contained absorption for the Si–Me and Si–Cl bonds and for the $Si–Cl_2$ group at 1270, 460, and 560 cm^{-1}, respectively. Thus, a characteristic feature of the IR spectra

TABLE 1. Physicochemical Constants and Chemical Shifts of Methyl Protons in 1,1,11,11-Tetrachlorodecamethylhexasiloxane, 2,4,4,6,6,8,8-Heptamethyl-2-(dichloropolymethylsiloxy)tetrasiloxanes, and 2,4,4,6,6,8,8-Heptamethyl-2-(chloro(hydroxy)-polymethylsiloxy)tetrasiloxanes

Compound	Yield, %	bp, °C (p, torr)	n_D^{25}	Empirical formula	Found/Calculated, %				$[M-CH_3]^+$/Mol. wt.	Number of Si atoms	δ, ppm
					C	H	Si	OH/Cl			
(Ia)	70,0	131–133 (3–4)	1,4009	$C_{10}H_{30}Si_6O_5Cl_4$	22,11/22,21	5,47/5,59	29,77/31,17	26,00/26,23	524/540,6	1,11 3,9 5,7	0,775 0,193 0,109
(IIa)	43,7	90–93 (3–4)	1,4085	$C_{10}H_{30}Si_6O_6Cl_2$	24,61/24,73	6,17/6,22	34,56/34,69	14,30/14,60	479/485,7	2 4,8 a b 6 a b (2) (4)	0,111 0,096 0,116 0,085 0,092 0,210 0,778
(IIb)	55,5	156–158 (5–6)	1,4070	$C_{14}H_{42}Si_8O_8Cl_2$	26,37/26,52	6,59/6,67	35,21/35,44	10,53/11,18	617/634,0	2 4,8 a b 6 a b (2) (4) (6) (8)	0,084 0,088 0,107 0,082 0,088 0,099 (0,109) 0,109 (0,099) 0,192 0,773
(IIc)	92,0	225–230	1,4040	$C_9H_{27}Si_5O_5Cl$	27,19/27,63	6,85/6,96	35,43/35,90	8,61/9,06	375/391,2	2 4,8 a b 6 a b (2)	0,131 0,098 0,126 0,085 0,098 0,461
(IId)	75,0	108–110 (2–3)	1,4050	$C_{13}H_{39}Si_7O_7Cl$	28,61/28,94	7,15/7,29	36,18/36,44	6,37/6.57	523/539,5	2 4,8 a, b 6 a, b (2) (4) (6)	0,085–0,110 0,106 0,132 0,447
(IIe)	74,8	74–75 (2–3)	1,4076	$C_9H_{28}Si_5O_6$	29,30/29,00	7,63/7,57	37,21/37,68	4,28/4,56	–/372,7	2 4,8 a b 6 a b (2)	0,097 0,097 0,120 0,086 0,097 0,141
(IIf)	84,5	104–105 (2–3)	1,4091	$C_{13}H_{40}Si_7O_8$	30,11/29,97	7,85/7,74	37,41/37,73	2,90/3,26	–/521,1		

of compounds of structure (II) [2,4,4,6,6,8,8-heptamethyl-2-(2,2,4-trimethyl-4,4-dichlorodisiloxy)tetrasiloxane and 2,4,4,6,6,8,8-heptamethyl-2-(2,2,4,4,6,6,8-heptamethyl-8,8-dichlorotetrasiloxy)tetrasiloxane] is the presence of two absorption bands for ν_{as} of the Si–O bond at 1040-1050 and 1090 cm^{-1}.

The chemical shifts (CS) of the PMR spectra of compounds with structures (I) and (II) are shown in Table 1. The spectra of the methyl protons of the cyclic moiety of the compounds of structure (II) are of a general nature. As a result of the symmetry of the molecule (the plane of symmetry is perpendicular to the plane of the ring and passes through Si^2 and Si^6), fragments Si_4Me_2 and Si_8Me_2 are enantiotopic.



$R = O(Me_2SiO)_nSiMeCl_2$; $(OMe_2Si)_nOH$; $(OMe_2Si)_n Cl$; $n = 1, 3$.

They contain two pairs of enantiotopic methyl groups (MG) Me^{4a}, Me^{8a}, and Me^{4b}, Me^{8b}, which differ in their spatial relationship to the substituent R (as a result of inadequate data, it was not possible to assign the signals to cis- or trans-methyl groups), and accordingly give rise to two signals. The Mg at Si^6 is invariant to symmetry operations, and also corresponds to two signals. The CS of the protons of the two MG at $Si^4(Si^8)$ and Si^6 are different, and are spin-coupled to the protons of the geminal MG ($^4J_{HCSiCH} = 0.4$ Hz). The signals for these MG are quartets. The signal for the protons of the MG at Si^2 is a singlet, since no adjacent proton-containing group is present. Hence, the cyclic moiety of the molecule gives rise to a singlet for Me^2 and quartets for $Me^{4a,8a}$, $Me^{4b,8b}$, Me^{6a}, and Me^{6b}, with integral intensities 1:2:2:1:1. The signals for the linear region of the molecule (II) are singlets, since the MG in $SiMe_2$ are symmetrical relative to the plane of symmetry of the molecule. Assignment of the $SiMe_2$ signals for the linear portion of compounds (IIa, b) and (IId) was made allowing for the influence of the Cl atoms. The protons of the MG adjacent to the Cl atom experience a greater low-field shift.

The functional methylcyclohexa(hepta, and octa)siloxanes were synthesized by the condensation of 1,1,9,9-tetrachlorooctamethylpentasiloxane or 1,1,11,11-tetrachlorodecamethylhexasiloxane with dimethylsilane or DHMDS. The compounds isolated were identified from their PMR, IR, and mass spectra and their elemental analyses as 2,6- and 2,8-dichloromethylcyclohexa(hepta, and octa)siloxanes of structure (III).

It is noteworthy that in the previously published IR spectra of dichloromethylcyclotetra(penta-, and hexa)siloxanes [1], and those of the newly-obtained dichloromethylcyclohepta(and octa)siloxanes, only one absorption band is present in the ν_{as} Si–O region, this being shifted from 1110 cm^{-1} in 2,6-dichloro-2,4,4,6,8,8-hexamethylcyclotetrasiloxane to 1070 cm^{-1} in 2,8-dichloro2,4,4,6,6,8,10,10,12,12,14,14,16,16-tetradecamethylcyclooctasiloxane beginning with dichlorodecamethylcycloheptasiloxane a shoulder appears at 1100-1110 cm^{-1}. A similar shift of the Si–O absorption has been observed previously in methylcyclosiloxanes [2].

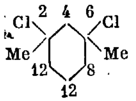
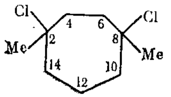
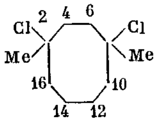
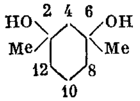
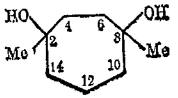
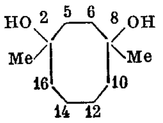
The CS of compounds of structure (III) have been reported [3]. The PMR spectra showed that the fractions isolated consisted of compounds of structure (III) only, no structural isomers of these compounds containing $MeSiCl_2$ groups having been formed.

The PMR spectra of the model compounds synthesized (IIa, b) and (IIIa, c) enabled the products of the reactions of 1,1,5,5-tetrachlorotrisiloxane and 1,1,9,9-tetrachlorooctamethylpentasiloxane with DHMTS to be identified. It was shown that compounds of structure (II) were formed [compounds (IIa, b)]. The molar proportions of these compounds lay between 0.08 and 0.15, this proportion increasing as the chain length of the initial α,α,ω,ω-tetrachlorodimethylsiloxane increased.

Hydrolysis of the dichloromethylcyclohexa(hepta, octa)siloxanes affords the respective dihydroxy-compounds, shown in Table 2 [compounds (IIId-f)].

Hence, the condensation of α,α,ω,ω-tetrachlorodimethylsiloxane with DHMTS involves two separate intramolecular cyclizations, resulting in the formation of the dichloromethylcyclosiloxanes and their structural isomers heptamethyl(dichloropolymethylsiloxy)cyclotetrasiloxanes, the separation of which by conventional methods is difficult. Our results show, how-

TABLE 2. Physicochemical Constants of Functional Methylcyclohexa(hepta-, and octa)siloxanes

Compound	Yield, %	bp, °C (p, torr)	n_D^{25}	Empirical formula	Found/Calculated, %				[M−CH₃]+ Mol. wt.
					C	H	Si	Cl/OH	
 (IIIa)	26,0	66–67 (3·10⁻²)	1,4103	$C_{10}H_{30}Si_6O_6Cl_2$	25,30 24,72	6,08 6,22	33,35 34,70	13,89 14,60	469 485,7
 (IIIb)	18,8	115–117 (5–6)	1,4112	$C_{17}H_{36}Si_7O_7Cl_2$	25,57 25,74	6,35 6,48	35,01 35,11	11,85 12,66	543 559,9
 (IIIc)	15,1	110–112 (0,5)	1,4114	$C_{14}H_{42}Si_8O_8Cl_2$	27,30 26,52	6,83 6,67	35,40 35,44	10,34 11,18	617 634,1
 (IIId)	66,2	105–107 (2·10⁻³)		$C_{10}H_{32}Si_6O_8$	27,10 26,75	7,15 7,18	37,01 37,55	7,36 7,58	– 448,9
 (IIIe)	55,7	110–112 (1)	1,4128	$C_{12}H_{38}Si_7O_9$	28,39 27,56	7,32 7,33	37,20 37,59	6,01 6,50	– 523,0
 (IIIf)	66,5	127–130 (0,5)	1,4119	$C_{14}H_{44}Si_8O_{10}$	28,46 28,16	7,56 7,42	37,89 37,63	5,40 5,96	– 597,19

ever, that dichloromethylcyclosiloxanes of varying ring sizes can be obtained by reacting α,α,ω,ω-tetrachloropolydimethylsiloxanes with dimethylsilanediol or DHMDS. In this case, intramolecular cyclization to give the structural isomers (pentamethyl(dichloropolymethylsiloxy)cyclotrisiloxanes) does not occur.

EXPERIMENTAL

PMR spectra were obtained in $CDCl_3 + CCl_4$ solution on a Bruker-WP-200SY NMR Fourier spectrometer, and IR spectra on a UR-20 spectrophotometer. Mass spectra were recorded on an AEI-MS-30 instrument (England), with the DS-50 data treatment system. The ionizing electron energy was 70 eV, emission current 100 mA, temperature of direct introduction system 30°C.

1,1,11,11-Tetrachlorodecamethylhexasiloxane (Ia). To a solution of 119 g (0.80 mole) of $MeSiCl_3$ in 250 ml of dry ether was added with stirring and cooling at −5°C over 4 h 42 g (0.122 mole) of 1,7-dihydroxyoctamethyltetrasiloxane and 22.8 g (0.244 mole) of aniline in 250 ml of dry ether. The precipitated aniline hydrochloride was filtered off, and the solvent removed. Distillation of the product (67 g) gave 50.7 g (70.0%) of (Ia). The physicochemical constants and the CS for the PMR spectrum are not shown in Table 1.

1,1,9,9-Tetrachlorooctamethylpentasiloxane (Ib) was obtained similarly, and its physicochemical constants have been reported previously [1].

Reaction of (Ib) with DHMTS. To 100 ml of dry ether were added simultaneously with stirring and cooling at −5°C 58.2 g (0.125 mole) of (Ib) in 250 ml of dry ether and 30 g (0.125 mole) of DHMTS and 23.3 g (0.250 mole) of aniline in 250 ml of dry ether. After a few days, the solid was filtered off, and the solvent removed. Fractionation of the product (75.6 g) gave: 11 g (13.9%) of (Ib), bp 80-83°C ($4 \cdot 10^{-2}$ torr), 19 g (24.4%) of a product bp 120-123°C ($3 \cdot 10^{-3}$ torr), which from its PMR spectrum was a mixture of 2,10-dichlorotetradecamethylcyclooctasiloxane and (IIb) in a ratio of 1:2 respectively, mass spectrum (m/z): 617 $[M - CH_3]^+$, 563 $[M - Cl - HCl]^+$, 471 $[563 - Me_2SiO_2]^+$, 415 $[563 - Me_2SiO_2]^+$, 401 $[415 - CH_2]^+$, 327 $[401 - Me_2SiO]^+$, 241 $[Me_6Si_3O_2Cl]^+$, 167 $[Me_4Si_2OCl]^+$, 147 $[Me_5Si_2O]^+$, 73 $[Me_3Si]^+$; and 9.4 g (11.9%) of (IVb), bp 140-142°C ($1 \cdot 10^{-2}$ torr), n_D^{20} 1.4058. Found, %: C 30.30; H 7.61; Si 37.91. $[M - CH_3]^+ = 785$. $C_{20}H_{60}Si_{11}O_{12}$. Calculated, %: C 30.00; H 7.50; Si 38.50. Mol. wt. 801.6.

2,8-Dichloro2,4,4,6,6,8,10,10,12,12,14,14,16,16-tetradecamethylcyclooctasiloxane (IIIc). To 150 ml of dry ether was added simultaneously with stirring at ~20°C 44.5 g (0.082 mole) of (Ia) in 250 ml of dry ether and 13.8 g (0.082 mole) of DHMDS and 15.4 g (0.165 mole) of aniline in 250 ml of dry ether. After two hours, the solid was filtered off and the solvent removed. Fractional distillation of the product (51.3 g) gave 7.8 g (15.1%) of (IIIc). For the physicochemical constants, see Table 2, and for the chemical shifts of the methyl protons, see [3].

Compounds (IIIa, b) were obtained similarly by the reaction of (Ib) with dimethylsilanediol, and (Ib) with DHMDS.

Hydrolysis of (IIIc). To 0.16 g (9 mmole) of water and 0.84 g (9 mmole) of aniline in 10 ml of ether was added 2.4 g (3.8 mmole) of (IIIc) in 15 ml of ether, with stirring at ~20°C. After two hours, the solid was filtered off and the ether removed. Fractionation of the product (2.25 g) gave 1.5 g (66.5%) of (IIIf). For physicochemical constants, see Table 2.

Compounds (IIId) and (IIIe) were obtained similarly.

2,4,4,6,6,8,8-heptamethyl-2-(2,2,4-trimethyl-4,4-dichlorodisiloxy)cyclotetrasiloxane (IIa). To 31 g (0.24 mole) of Me_2SiCl_2 in 100 ml of dry ether was added 18.2 g (0.061 mole) of hydroxyheptamethylcyclotetrasiloxane and 5.7 g of aniline in 200 ml of dry ether. On the following day, the solid was filtered off, and the ether removed. Fractionation of the product (26 g) gave 22.1 g (92.0%) of (IIc) (physicochemical constants given in Table 1). Compound (IId) was obtained similarly, by reacting heptamethyl(hydroxy)cyclotetrasiloxane with 1,5-dichlorohexamethylsiloxane. To 1.08 g of water (0.06 mole) and 6.5 g (0.07 mole) of aniline in 250 ml of ether was added with stirring over 1 h at 20-22°C 20.8 g (0.053 mole) of (IIc). The solid was filtered off, the ether solution washed with water, and the ether evaporated. Fractionation of the product (19.6 g) gave 14.8 g (74.8%) of (IIe). Physicochemical constants and CS of the methyl protons given in Table 1.

Compound (IIf) was obtained similarly.

To 37.4 g (0.25 mole) of $MeSiCl_3$ in 200 ml of dry ether was added with stirring at 20-22°C 18.3 g (0.049 mole) of (IIe) and 4.5 g (0.049 mole) of aniline in 100 ml of dry ether. After a few hours, the solid was filtered off, and the solvent and excess Me_2SiCl_2 distilled off. Fractionation of the product (19.6 g) gave 10.4 g (43.7%) of (IIa). (IIb) was obtained similarly. The physicochemical constants and the CS for the PMR spectra for (IIa, b) are given in Table 1.

CONCLUSIONS

1. Condensation of α,α,ω,ω-tetrachlorodimethylsiloxane with 1,5-dihydroxyhexamethyltrisiloxane involves two intramolecular cyclizations, resulting in the formation of dichloromethylcyclosiloxanes and heptamethyl(dichloropolymethylsiloxy)cyclotetrasiloxanes, their structural isomers. The proportion of heptamethyl(dichloropolymethylsiloxy)cyclotetrasiloxanes increases as the length of the α,α,ω,ω-tetrachlorodimethylsiloxanes increases.

2. Difunctional methylcyclohexa(hepta-, and octa)siloxanes are obtained by condensing α,α,ω,ω-tetrachlorodimethylsiloxanes with dimethylsilanediol and 1,3-dihydroxytetramethyldisiloxane.

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REACTION OF $[Pt(CO)_2]_n$ WITH TRIARYLPHOSPHINES

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We have previously obtained tetra- and pentanuclear clusters of Pt by reacting controlled amounts of triethylphosphine with a solution of platinum dicarbonyl in acetone [1], and we observed that the amount of NH_3 introduced into the system affected the selectivity of the reaction. We here report an extension of this method of synthesis to trianylphosphines PAr_3, and progress has been made towards an understanding of the mechanism of the reaction of $[Pt(CO)_2]_n$ solutions with tertiary phosphines.

EXPERIMENTAL

All operations were carried out under CO or N_2. The platinum dicarbonyl solutions were obtained as described in [1]. In order to study the IR spectra of the solutions, the original aqueous—ethanolic solutions of platinum dicarbonyl containing NH_3 were treated with the required amount of trioctylbenzylammonium chloride, followed by extraction with dichloromethane. The extract was washed with water, dried over $MgSO_4$, the dichloromethane removed under reduced pressure, and the dry residue dissolved in tetrahydrofuran (THF).

Preparation of $Pt_5(CO)_6(PAr_3)_4$. To an aqueous—acetone solution of $[Pt(CO)_2]_n$ was added PAr_3(Pt/PAr_3 ratio = 1:1), and the mixture was kept for one day under CO. The acetone was then distilled off under reduced pressure, and the residue recrystallized from a mixture of benzene and ethanol. The compound was purified by chromatography on a silica gel column, eluent benzene.

Preparation of $Pt_3(CO)_3(PAr_3)_4$. To an aqueous—ethanolic solution of $[Pt(CO)_2]_n$ was added a solution of PAr_3 (molar ratio Pt/PAr_3 = 1:1.33), and the mixture stirred in air for 0.5 h. The solid which separated was then filtered off and recrystallized from a mixture of acetone and ethanol.

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