Anal. Calcd. for $C_{26}H_{20}O$: C, 89.7; H, 5.7. Found: C, 89.4; H, 5.9.

Oxidation.—The carbinol (0.7 g.) was oxidized with chromic acid (0.66 g.) as described above. The yellow product crystallized spontaneously on cooling; from acetic acid orange prisms, m. p. 194° (III, R = CH_3).

Anal. Calcd. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.5. Found: C, 86.0; H, 5.8.

Ethylenization.—The carbinol (1.5 g.) was refluxed for seventy-five hours with a mixture of acetic acid (155 cc.) and 48% hydrobromic acid (15 cc.). The ethylene (II, R = CH_3) formed brown, square plates, m. p. 236–237° (from xylene).

Anal. Calcd. for $C_{52}H_{36}$: C, 94.5; H, 5.5. Found: C, 94.9; H, 5.2.

Summary

1. Diarylcarbinols with two ortho substituents in one aryl group such as (9′-phenanthryl)-(2-ethoxy-naphthyl-1)-carbinol or (9′-phenanthryl)-(2-methyl-naphthyl-1)-carbinol are converted quantitatively into ethylenes by strong mineral acids.
2. The mechanism of the formation of tetraarylethylenes is represented as involving electrophilic substitution, by a diarylcarbonium ion, of the α-hydrogen of the diarylcarbinol or its ether.
3. Oxidation in acetic acid solution of diarylcarbinols with at least three of the four ortho positions substituted, yields hydrated ketones or their acetylation products.

REHOVOTH, PALESTINE RECEIVED OCTOBER 10, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Thermal Rearrangement of Branched-Chain Methylpolysiloxanes[1]

BY DONALD W. SCOTT

The higher molecular weight dimethylsilicone polymers obtained by hydrolysis of dimethyldichlorosilane have been found by Patnode[2] to undergo thermal rearrangement readily to give lower molecular weight cyclic structures, $[(CH_3)_2SiO]_n$. In the present work it has been found that branched-chain methylpolysiloxanes obtained by co-hydrolysis of dimethyldichlorosilane with methyltrichlorosilane and with silicon tetrachloride likewise undergo thermal rearrangement to yield lower molecular weight methylpolysiloxanes. From the products of such thermal rearrangements a total of ten new methylpolysiloxane compounds have been isolated.

Experimental

Thermal Rearrangement of the Co-hydrolysis Product of Dimethyldichlorosilane and Methyltrichlorosilane.—To a vigorously stirred, two-phase mixture of six liters of water, 1200 g. of butanol, and 600 g. of toluene was slowly added a mixture of 830 g. (6.4 moles) of dimethyldichlorosilane, 970 g. (6.4 moles) of methyltrichlorosilane and 600 g. of toluene. (Such a co-hydrolysis in the presence of a butanol–toluene mixture eliminates or greatly reduces the formation of insoluble gel.[3]) The organic layer was separated from the aqueous phase and washed free of acid, after which the toluene and butanol were removed by distillation under reduced pressure. The product so obtained was a viscous, translucent liquid. This material was heated in a Claisen flask, through which was passed a slow stream of nitrogen. Below 350° no distillate was obtained, indicating that little or no low molecular weight, volatile material was present. Above 350° thermal rearrangement commenced and distillate came over steadily as the temperature was raised slowly. At about 450° the contents of the flask formed a gel which, however, continued to undergo thermal rearrangement as the temperature was raised slowly to a final value of 600°. In this manner approximately two-thirds of the original co-hydrolysis product was converted to volatile material, the remainder having been left in the bulb of the Claisen flask as a brittle solid.

The distillate collected was a mixture of amber colored liquid and a very small amount of a white crystalline solid. This crystalline material was found to be practically insoluble in hydrocarbon solvents and to sublime above 200°. Purification was accomplished by extraction with toluene followed by sublimation under reduced pressure. This compound is listed in Table I, which follows, as compound F. The remainder of the volatile product was distilled in a fractionating column, taking over all material boiling below 260°. In the boiling point range below 200° the only compounds found were $[(CH_3)_2SiO]_3$ and $[(CH_3)_2SiO]_4$.[2] Most of the distillation cuts in the boiling point range 200–260° deposited crystalline material when allowed to stand in a refrigerator for several days. By fractional crystallization, usually using toluene as solvent, five pure crystalline compounds were isolated from these distillation cuts. These five compounds are listed in Table I, compounds A to E inclusive.

The six compounds isolated from the thermally rearranged material were analyzed, and cryoscopic molecular weight determinations were made for all except compound F. Included in Table I are the empirical formulas found for these six compounds, their melting and boiling points, and the analytical and molecular weight data on which their identification is based.

The yield of each of these compounds was low—in all cases less than one per cent. of the original polymeric material subjected to thermal rearrangement. This is a consequence of the large number of possible compounds which can be formed by such a thermal rearrangement, so that the amount of any one particular compound is a small part of the total product. Separation by fractional crystallization, as was done in this case, tends to isolate preferentially compounds with higher melting points; the material in the boiling point range 200–260° no doubt contained a number of other compounds with lower melting points which were not isolated.

Thermal Rearrangement of the Co-hydrolysis Product of Dimethyldichlorosilane and Silicon Tetrachloride.—To a vigorously stirred, two-phase mixture of six liters of water, 1200 g. of butanol and 600 g. of toluene was added slowly

---

[1] The nomenclature used in this article is based on the system of organosilicon nomenclature discussed by Sauer [*J. Chem. Ed.*, **21**, 303 (1944)]. The numbering of the more complex siloxane ring structures follows that accepted for carbon ring compounds (Patterson and Capell, "The Ring Index," Reinhold Publishing Co., New York, N. Y., 1940).

[2] W. I. Patnode, private communication.

[3] R. O. Sauer, private communication.

TABLE I

METHYLPOLYCYCLOPOLYSILOXANES

	Formula	M. p., °C.	B. p., °C.	% H		% C		% Si		Mol. wt.	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found[a]
A	$(CH_3)_8Si_5O_6$	118	203	6.78	6.8	26.95	26.4	39.35	39.2	356.6	361
B	$(CH_3)_{10}Si_6O_7$	51	232	7.02	7.0	27.88	28.7	39.09	38.2	430.7	437
C	$(CH_3)_8Si_6O_8$	119	220	5.81	5.9	23.06	23.0	40.41	39.9	416.6	409
D	$(CH_3)_{10}Si_7O_9$	150	248	6.16	6.3	24.47	24.6	40.02	39.7	490.8	495
E	$(CH_3)_{10}Si_8O_{11}$	139	257	5.49	5.4	21.81	22.5	40.75	39.8	550.8	550
F	$[CH_3SiO_{3/2}]_{2n}$	Sublimes without melting		4.51	4.5	17.90	17.4	...	...	Not determined, see text	

[a] Cryoscopically in cyclohexane.

TABLE II

METHYLSPIROPOLYSILOXANES

	Formula	M. p., °C.	B. p., °C.	% H		% C		% Si		Mol. wt.	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found[a]
G	$(CH_3)_8Si_5O_6$	121	204	6.78	6.6	26.95	26.4	39.35	39.3	356.6	370
H	$(CH_3)_{10}Si_6O_7$	57	230	7.02	6.9	27.88	27.7	39.09	38.6	430.7	429
I	$(CH_3)_{12}Si_7O_8$[b]	31	254	7.19	7.0	28.55	27.8	...	..	504.8	496
J	$(CH_3)_{14}Si_8O_9$[c]	−12	157 (20 mm.)	7.31	7.3	29.04	29.1	...	..	579.0	585

[a] Cryoscopically in cyclohexane. [b] For supercooled liquid, d^{20}_4 1.0352, n^{20}_D 1.4031, r_D 0.2358. [c] d^{20}_4 1.0260, n^{20}_D 1.4032, r_D 0.2379.

a mixture of 1425 g. (11 moles) of dimethyldichlorosilane, 375 g. (2.2 moles) of silicon tetrachloride and 600 g. of toluene. The organic layer was separated from the aqueous phase, washed free of acid, and centrifuged to remove traces of gel. Removal of the butanol and toluene by distillation under reduced pressure left the co-hydrolysis product as a translucent, viscous liquid. This material, when heated in a Claisen flask, behaved much the same as the co-hydrolysis product of dimethyldichlorosilane and methyltrichlorosilane described previously. Thermal rearrangement began at about 375° and continued as the temperature was gradually raised to 600°. The volatile material which distilled over corresponded to about two-thirds of the original co-hydrolysis product, the other third having remained in the bulb of the Claisen flask as a brittle, solid material.

The distillate collected was redistilled in a fractionating column. By fractional crystallization of the appropriate distillation cuts, four new compounds were isolated. These four compounds are listed in Table II, which gives their empirical formulas, melting and boiling points, and the analytical and molecular weight data on which their identification is based. The compounds $[(CH_3)_2SiO]_3$ and $[(CH_3)_2SiO]_4$[2] were also found to be present in this thermally rearranged material.

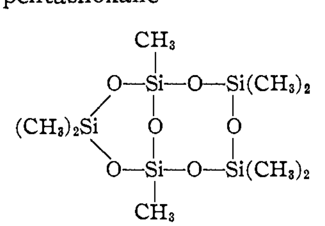
The yields of compounds G and H were low, in both cases less than one per cent. of the original polymeric material subjected to thermal rearrangement; the yields of compounds I and J were somewhat better, being 7% and 3%, respectively, of the starting material. The somewhat better yields of individual compounds in this case, as compared with the thermal rearrangement of the co-hydrolysis product of dimethyldichlorosilane and methyltrichlorosilane, can probably be attributed to the smaller number of possible compounds in a given boiling point range.

Mixed Melting Points.—Compounds A and G and also compounds B and H have the same empirical formulas and similar melting and boiling points. Mixed melting point determinations showed that they are actually different compounds.

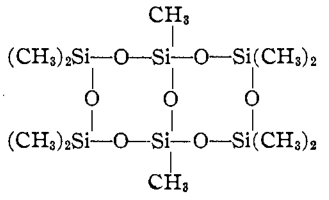
Discussion

Patnode[2] found in the products of thermal rearrangement of dimethylsilicone polymers at about 400° only the cyclic compounds $[(CH_3)_2SiO]_n$. This fact shows that silicon–oxygen bonds alone were involved in the thermal rearrangement, the silicon–carbon bonds having remained intact. Although in the present work the thermal rearrangements took place at a somewhat higher temperature, it seems a very reasonable assumption that here also silicon–oxygen bonds alone were involved, the methyl groups remaining attached to the silicon atoms. Assignments of structure to certain of the products of the thermal rearrangements are made on this basis.

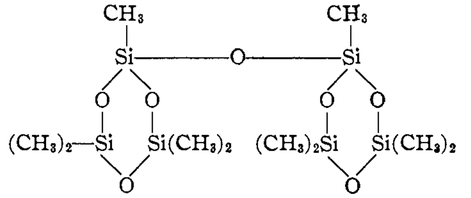
Methylpolysiloxanes resulting from co-hydrolysis of methyltrichlorosilane and dimethyldichlorosilane have silicon atoms bonded to either one or two methyl groups. If the silicon–carbon bonds remain intact during thermal rearrangement, the products will likewise have silicon atoms bonded to either one or two methyl groups. On this basis, compound A, $(CH_3)_8Si_5O_6$, is octamethylbicyclo[5.3.1]pentasiloxane



Compounds B, C, D and E cannot be assigned definite structural formulas because several isomeric structures correspond to the empirical formulas found for these compounds. To illustrate, two of the several possible structures for compound B, $(CH_3)_{10}Si_6O_7$, are

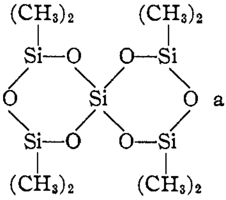


and

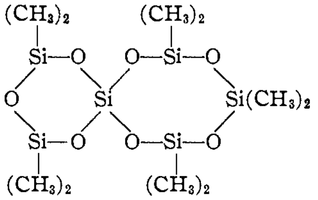


No attempt was made to determine which of several isomeric structures corresponded to the compounds actually obtained, since at present no simple straightforward means is available by which this might be done. Compound F had too low a solubility in any of numerous solvents tried to permit determination of its molecular weight by the cryoscopic method. Hence it was not completely characterized. The analytical data show that it is $[CH_3SiO_{3/2}]_{2n}$, where n is some integer. Thus each of its silicon atoms is bonded to only one methyl group. Its solubility behavior and the fact that it sublimes without melting, is indicative of a structure which can fit very compactly into the crystal lattice.

Methylpolysiloxanes resulting from co-hydrolysis of dimethyldichlorosilane and silicon tetrachloride have some silicon atoms which are bonded to two methyl groups and two oxygen atoms and some which are bonded to four oxygen atoms. If the methyl groups remain attached to the silicon atoms during thermal rearrangement, the products will likewise have silicon atoms bonded either to two methyl groups and two oxygen atoms or to four oxygen atoms. On this basis, compounds G and H, $(CH_3)_8Si_5O_6$ and $(CH_3)_{10}Si_6O_7$, respectively, are octamethylspiro[5.5]pentasiloxane and decamethylspiro[5.7]hexasiloxane



and



Compounds I and J cannot be assigned definite structural formulas because in each case two isomeric structures correspond to the empirical formula found. As before, no attempt was made to establish which of the two possible isomeric structures corresponded to the compound actually obtained.

Acknowledgment.—The analytical data listed in Tables I and II were obtained by Mr. L. B. Bronk of this Laboratory.

Summary

1. Six methylpolycyclopolysiloxanes have been prepared by thermal rearrangement of a co-hydrolysis product of dimethyldichlorosilane and methyltrichlorosilane.

2. Four methylspiropolysiloxanes have been prepared by thermal rearrangement of a co-hydrolysis product of dimethyldichlorosilane and silicon tetrachloride.

SCHENECTADY, N. Y. RECEIVED SEPTEMBER 11, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Methylpolysiloxanes[1]

BY WINTON PATNODE AND DONALD F. WILCOCK

The availability of the three methylchlorosilanes, $(CH_3)_3SiCl$, $(CH_3)_2SiCl_2$ and CH_3SiCl_3,[2] has prompted a further study of their products of hydrolysis, the methylpolysiloxanes and the methylchloropolysiloxanes. Sauer[3] has already described trimethyl silanol and its dehydration product, hexamethyldisiloxane, both derived from trimethylchlorosilane. Hyde and Delong[4] obtained a complex mixture of compounds by the hydrolysis of dimethyldichlorosilane, but did not report the isolation and purification of the compounds present, aside from an apparently cyclic trimer, $((CH_3)_2SiO)_3$. Rochow and Gilliam[5] described the resinous products produced by the co-hydrolysis of dimethyldichlorosilane and methyltrichlorosilane.

We have now studied more fully the methylpolysiloxanes derived from the methylchlorosilanes, as well as some of the reactions by which the polymers may be rearranged. The methylchlorosilanes used in this work were prepared by the reaction of methyl chloride on silicon according to the method of Rochow.[6] They were isolated from the reaction mixture by fractional distillation.

Hydrolysis of Dimethyldichlorosilane

When dimethyldichlorosilane is mixed with a large volume of water, hydrolysis occurs exothermally to form hydrochloric acid and an immiscible, colorless oil having an empirical composition close to $(CH_3)_2SiO$. Examination of this oil reveals that it contains cyclic polymers of the

---

(1) The nomenclature used throughout this paper follows the system proposed by R. O. Sauer, *J. Chem. Ed.*, **21**, 303 (1944).

(2) W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, THIS JOURNAL, **63**, 801 (1941); A. G. Taylor and B. V. deG. Walden, *ibid.*, **66**, 842 (1944); W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).

(3) R. O. Sauer, *ibid.*, **66**, 1707 (1944).

(4) J. F. Hyde and R. C. Delong, *ibid.*, **63**, 1194 (1941).

(5) E. G. Rochow and W. F. Gilliam, *ibid.*, **63**, 798 (1941).

(6) E. G. Rochow, *ibid.*, **67**, 963 (1945).