# The Selective Halogenation of Methylhydropolysiloxanes : Syntheses of Methylhalopolysiloxanes and Their Derivatives

By Minoru SAKIYAMA,[†] Yukinori NISHIZAWA
and Rokuro OKAWARA

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Toward nucleophilic reagents, the silicon-hydrogen bond is less reactive than Si–Cl, but more reactive than C–H. Thus, the hydrolysis of methylhydrochlorosilanes gives silicon-oxygen compounds with hydrogen still bonded to the silicon. Recently, we have reported on the synthesis of many organosiloxane polymers prepared by the co-hydrolysis of dimethylchlorosilane or methyldichlorosilane with other methylchlorosilanes.1) The reaction of some of these compounds with cupric oxide has also been reported on.2) In this

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[†] Present address: Department of Chemistry, Faculty of Science, Osaka University, Kita Toneyama, Toyonaka.

1) a) R. Okawara and M. Sakiyama, This Bulletin, **29**, 236, 547 (1956). b) R. Okawara, U. Takahashi and M. Sakiyama, ibid., **30**, 608 (1957). See also, R. Okawara and M. Sakiyama, *Technol, Rept. Osaka Univ.*, **7**, 459 (1957).

2) M. Sakiyama and R. Okawara, *J. Organometal. Chem.*, **2**, 473 (1964).

Table I. Linear and cyclic methylbromopolysiloxanes

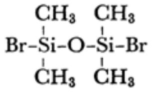
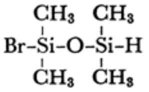
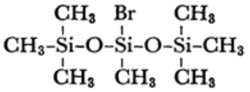
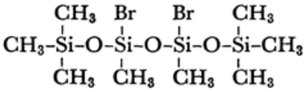
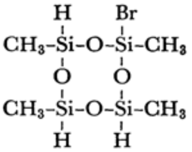
| | | Starting material | | | Product | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Methylhydro-polysiloxane g. (mol.) | $Br_2$ g. (mol.) | Pyridine g. (mol.) | Compound | wt. g. | % yield | B. p. °C/mmHg | %Br(-Si) Found (Calcd.) | $n_D^{20}$ |
| I | M'$_2$ | 40(0.3) | 96(0.6) | 48(0.6) |  $Br-Si(CH_3)_2-O-Si(CH_3)_2-Br$ | 30 | 70 | 167/760 | 53.3 (54.7) | — |
| II | M'$_2$ | 40(0.3) | 48(0.3) | 24(0.3) |  $Br-Si(CH_3)_2-O-Si(CH_3)_2-H$ | 14 | 22 | 122/760 | 35.1 (37.5) | — |
| III | MD'M | 89(0.4) | 64(0.4) | 32(0.4) |  $CH_3-Si(CH_3)_2-O-Si(CH_3)(Br)-O-Si(CH_3)_2-CH_3$ | 32 | 28 | 77/28 | 26.2 (26.6) | — |
| IV | MD'$_2$M | 16(0.06) | 18(0.12) | 9(0.12) |  $CH_3-Si(CH_3)_2-O-Si(CH_3)(Br)-O-Si(CH_3)(Br)-O-Si(CH_3)_2-CH_3$ | 7 | 28 | 114/12 | 35.2 (36.4) | — |
| V | D'$_4$ | 30(0.125) | 20(0.125) | 10(0.125) |  | 5 | 13 | 59—60/15 | 22.3 (24.8) | 1.4113 |

Table II. Co-hydrolysis of methyldichlorosilane and dimethyldichlorosilane

| | Starting material | | | Product | | Tetramer | Pentamer | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Expt. | $CH_3SiHCl_2$ mol. | $(CH_3)_2SiCl_2$ mol. | mole ratio | g. | %yield | g. | g. | % composition | | | | | |
| | | | | | | | | D'$_5$ | DD'$_4$ | $D_2$D'$_3$ | $D_3$D'$_2$ | $D_4$D' | $D_5$ |
| 1 | 0.8 | 2.4 | 1/3 | 180 | 80 | 88 | 24 | 0 | 0 | 0 | 38 | 44 | 17 |
| 2 | 1.6 | 1.6 | 1/1 | 190 | 88 | 93 | 34 | 0 | 11 | 37 | 40 | 9 | 3 |
| 3 | 2.4 | 0.8 | 3/1 | 155 | 77 | 65 | 27 | — | — | — | — | — | — |
| 4 | 3.2 | 0.0 | — | 85 | 44 | 32 | 14 | 100 | 0 | 0 | 0 | 0 | 0 |
| | | | | (not decomposed thermally) | | | | | | | | | |

Table III. Methylhydrocyclopentasiloxanes

| Compound | B. p. °C/mmHg | $n_D^{20}$ | $d_4^{20}$ | $MR_D$ c) Found (Calcd.) | %H(-Si) Found (Calcd.) |
|---|---|---|---|---|---|
| D'$_5$ a) | 168.7 | 1.3912 | 0.9985 | 71.54(71.35) | — |
| DD'$_4$ | — | — | — | — | — |
| $D_2$D'$_3$ | 81/18 | 1.3942 | 0.9794 | 80.32(80.09) | 0.92(0.92) |
| $D_3$D'$_2$ | 88/18 | 1.3957 | 0.9726 | 84.62(84.46) | 0.60(0.57) |
| $D_4$D' | 96/18 | 1.3970 | 0.9662 | 88.92(88.83) | 0.27(0.28) |
| $D_5$ b) | 210 | 1.3982 | 0.9593 | 93.40(93.20) | — |

a) R. O. Sauer, W. J. Scheiber and S. D. Brewer, *J. Am. Chem. Soc.*, **68**, 962 (1946).

b) W. I. Patnode and D. F. Wilcock, ibid., **68**, 358 (1946).

c) Calculated from bond refractivities by E. L. Warrick, ibid., **68**, 2455 (1946).

Table IV. Bromination of methylhydrocyclotetra- and -pentasiloxanes

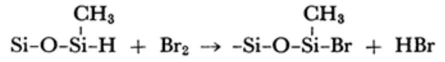
| | Starting material | | | | | Product | |
|---|---|---|---|---|---|---|---|
| Expt. | Main component | B. p. °C/mmHg | $n_D^{20}$ | %H(-Si) | wt. g. | wt. g. | % yield |
| 1 | $D_3$D' | 64—66/20 | 1.3935—1.3940 | 0.53—0.45 | 25.5 | 18.1 | 39 |
| 2 | $D_2$D'$_2$ | 56—60/20 | 1.3918—1.3822 | 0.84—0.72 | 23.4 | 10.3 | 29 |
| 3 | DD'$_3$ | 48—55/20 | 1.3901—1.3911 | 1.02—0.94 | 23.0 | 17.0 | 45 |
| 4 | D'$_4$ | 132/760 | 1.3870 | 1.67 | 13.0 | 6.7 | 17 |
| 5 | $D_4$D' | 92—99/20 | 1.3969—1.3972 | 0.19—0.44 | 13.8 | 8.6 | 38 |

paper, we will report on the preparation of methylhalopolysiloxanes obtained by the halogenation of these polymers.

In these reactions, it is necessary to use a reagent which will halogenate the silanic hydrogen without reacting with the C–H and Si–O bonds. Photochlorination in a cooled carbon tetrachloride was applied successfully to $D'_n$ ($n=4-7$)* in order to chlorinate the silanic hydrogen.³⁾ However, this method brings about the chlorination of the methyl hydrogen when applied to the methylchlorosilanes, $M_2$ and $D_4$.⁴⁾ Moreover, in the case of $M_2$, the Si–O bond cleaved by hydrogen chloride. Elemental bromine readily reacts with alkylsilanes, for example, diethylsilane, to form alkylsilyl bromides.⁵⁾ However, bromine is unreactive toward hexamethyldisiloxane or alkylchlorosilanes not containing Si–H, except under forcing conditions.⁶⁾ Thus, bromine seemed a good choice as a reagent for the selective bromination of methylhydropolysiloxanes.

Photo-chlorination by chlorine gas by the method of Sokolov et al.³⁾ was first examined. $M'_2$ reacted with chlorine, but an aqueous layer soon separated, and much more chlorine was absorbed than had been calculated. It is evident that the carbon-hydrogen and silicon-oxygen bonds were attacked by, respectively, the chlorine and hydrogen chloride formed, in contrast to the case of $D'_n$. Bromine did not react with $M_2$ and $D_4$, even when refluxed, but did react violently with $M'_2$, the brown color disappearing soon after the addition. $D'_4$ also reacted with bromine, though less vigorously than $M'_2$. In both cases, however, the corresponding silicon-brominated compounds were obtained in only poor yields. A cleavage of the silicon-oxygen bond by hydrogen bromide probably takes place in these cases.

Pyridine forms crystalline adducts with bromine. The adducts are so unstable, however, that they decompose into bromine and pyridine when exposed to air.⁷⁾ Thus, pyridine may be expected to be utilized successfully in order to prevent the cleavage of the silicon-oxygen bond resulting from the attack of hydrogen bromide by forming pyridine hydrobromide. When bromine was added to a mixture of methylhydropolysiloxane and pyridine dissolved in carbon tetrachloride, the reaction took place smoothly and the corresponding bromo - compounds were obtained. The reaction scheme is as follows:



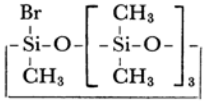
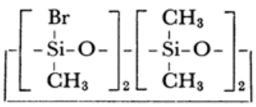
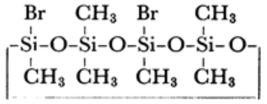
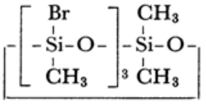
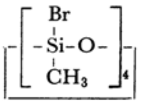
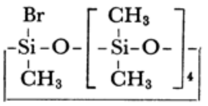
$$\text{Si-O-}\overset{\text{CH}_3}{\text{Si}}\text{-H} + Br_2 \rightarrow \text{-Si-O-}\overset{\text{CH}_3}{\text{Si}}\text{-Br} + HBr$$

$$HBr + C_5H_5N \rightarrow C_5H_5NH^+Br^-$$

By this method the bromine-substituted methylpolysiloxanes given in Table I were synthesized. Iodine and iodine chloride were found to react neither with $M'_2$ nor with $D'_4$.

In the preceding paper, the isolation of methylhydrocyclotetrasiloxanes, $D_3D'$, $D_2D'_2$, $DD'_3$ as well as $D'_4$, was reported from the co-hydrolysis of methyldichlorosilane and dimethyldichlorosilane.¹ᵇ⁾ In the present experiments, the isolation of methylhydrocyclopentasiloxanes was attempted, and $D_4D'$, $D_3D'_2$, and $D_2D'_3$ were obtained. Details of the reaction and the properties of these polysiloxanes are presented on Tables II and III. Fractions of the above-mentioned co-hydrolyzate, fractions which are composed mainly of $D'_4$, $DD'_3$, $D_2D'_2$, $D_3D'$, and $D_4D'$ respectively, were perfectly brominated in the presence of pyridine. Details of the reactions and properties of the methylbromopolysiloxanes thus obtained are given in Tables IV and V.

TABLE V. CYCLIC METHYLBROMOPOLYSILOXANES

| Compound | B. p. °C/mmHg | M. p. °C | %Br (-Si) Found (Calcd.) |
|---|---|---|---|
|  | 68/18 | — | 21.2<br>(22.1) |
| <br>and/or<br> | 107/20 | 49 | 37.2<br>(37.5) |
|  | 92/55 | 58—59 | 47.4<br>(48.8) |
|  | 112/ 4 | 97—98 | 56.8<br>(57.5) |
|  | 90/ 4 | — | 18.2<br>(18.4) |

Mono-bromine- or -chlorine-substituted methylpolysiloxanes synthesized as described above, or by the analogous method of Sokolov et al.,³⁾ were hydrolyzed or co-hydrolyzed with trimethylchlorosilane and dimethylchlorosilane in a large amount of water. Details of the experiments are given in Table VI. In the co-hydrolysis experiments,

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* In order to show the structural units of methylpolysiloxanes, short-hand notations, which have been used frequently, will be used in this paper as follows:

$(CH_3)_3SiO_{1/2}$ : M, $O_{1/2}Si(CH_3)_2O_{1/2}$ : D,
$H(CH_3)_2SiO_{1/2}$ : M′, $HSi(CH_3)O_{2/2}$ : D′.

3) N. N. Sokolov, K. A. Andrianov and S. M. Akimova, *Zhur. Obshchei Khim.*, **26**, 933 (1956).

4) F. C. Whitmore and L. H. Sommer, *J. Am. Chem. Soc.*, **68**, 481 (1946); R. H. Krieble and J. R. Elliott, ibid., **67**, 1810 (1945); B. A. Bluestain, ibid., **70**, 3068 (1948).

5) P. A. McCusker and E. L. Reilly, ibid., **75**, 1583 (1953).

6) J. R. Speier, Jr., ibid., **73**, 826 (1951).

7) P. F. Trowbridge and O. C. Diehl, ibid., **19**, 562 (1898).

TABLE VI. HYDROLYSIS OF HALOGEN SUBSTITUTED METHYLPOLYSILOXANES

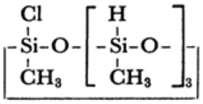
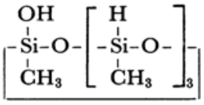
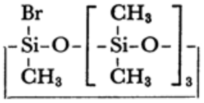
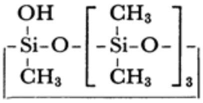
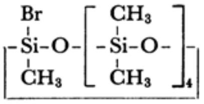
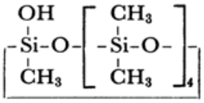
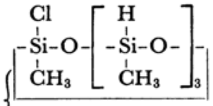
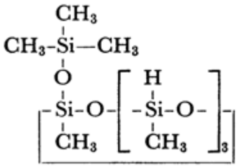
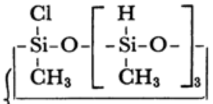
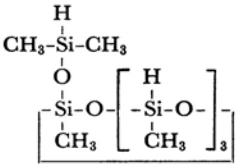
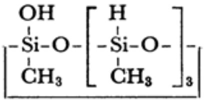
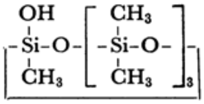
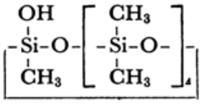
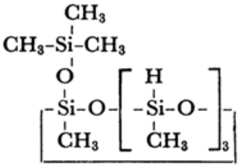
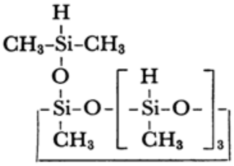
| Starting material | | Product | | | | |
|---|---|---|---|---|---|---|
| Compound | wt. g. | Compound | wt. g. | Yield % | %OH Found (Calcd.) | %H(—Si) Found (Calcd.) |
|  $\overset{\mathrm{Cl}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 33 |  $\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 3 | 10 | — | 1.16<br>(1.16) |
|  $\overset{\mathrm{Br}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 14 |  $\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 5 | 41 | 5.69<br>(5.70) | — |
|  $\overset{\mathrm{Br}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_4$ | 3.4 |  $\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_4$ | 1.5 | 50 | 4.58<br>(4.56) | — |
|  $\overset{\mathrm{Cl}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$<br>$(\mathrm{CH_3})_3\mathrm{SiCl}$ | 20<br>40 |  $\underset{\mathrm{CH_3}}{\overset{\overset{\mathrm{CH_3-\overset{CH_3}{Si}-CH_3}}{\mathrm{O}}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 2 | 8 | — | 0.90<br>(0.91) |
|  $\overset{\mathrm{Cl}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$<br>$\mathrm{H(CH_3)_2SiCl}$ | 27<br>40 |  $\underset{\mathrm{CH_3}}{\overset{\overset{\mathrm{CH_3-\overset{H}{Si}-CH_3}}{\mathrm{O}}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 9 | 29 | — | 1.25<br>(1.27) |

TABLE VII. PROPERTIES OF METHYLHYDROXYPOLYSILOXANES

| Compound | B. p. °C/mmHg | $n_D^{20}$ | $d_4^{20}$ | MR$_D$* Found (Calcd.) |
|---|---|---|---|---|
|  $\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 76/10 | 1.4040 | — | — |
|  $\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 80/ 9 | 1.4076 | 1.0404 | 70.76<br>(70.47) |
|  $\overset{\mathrm{OH}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_4$ | 92/3.8 | 1.4077 | 1.0273 | 89.46<br>(89.11) |
|  $\underset{\mathrm{CH_3}}{\overset{\overset{\mathrm{CH_3-\overset{CH_3}{Si}-CH_3}}{\mathrm{O}}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 68/10 | 1.3963 | — | — |
|  $\underset{\mathrm{CH_3}}{\overset{\overset{\mathrm{CH_3-\overset{H}{Si}-CH_3}}{\mathrm{O}}}{-\mathrm{Si}-\mathrm{O}-}}\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{-\mathrm{Si}-\mathrm{O}-}}\right]_3$ | 67/10 | 1.3922 | — | — |

* See Ref. c of Table III.

hydroxy-substituted methylcyclotetrasiloxanes were also formed. The properties of the siloxanols thus obtained are given in Table VII.

## Experimental

**Starting Materials.**—The preparation of the methylhydropolysiloxanes used in these experiments has already been reported on.[1]

**Bromination.**—Into a mixture of methylhydropolysiloxane and pyridine, dissolved in carbon tetrachloride and placed in a three-necked flask equipped with an efficient stirrer, a reflux condenser and a dropping funnel, bromine, diluted with carbon tetrachloride was stirred. After the addition, the mixture was refluxed for 30 to 60 min. in order to complete the reaction. Pyridine hydrobromide was then filtered off, and the filtrate was fractionally distilled. Hydrolyzable bromine was analyzed by neutralizing the hydrogen bromide formed from the hydrolysis of the methylbromopolysiloxanes.

**Co-hydrolysis.** — Methylhalogenopolysiloxanes or mixtures of them with methylchlorosilanes, diluted with dry ether, was added to cooled water. In the case of siloxanol formation, a buffer solution was used, and the mixture was neutralized by a dilute alkaline solution in the course of the reaction. The ethereal layer was separated, and, after the ether had been distilled off, the residue was fractionated by the column described in the previous papers. The hydroxyl content was determined with a Karl Fischer reagent.

## Summary

Bromine was utilized in the presence of stoichiometric amount of pyridine to brominate silanic hydrogen of methylhydropolysiloxanes. Methylbromopolysiloxanes thus obtained and methylchloropolysiloxanes prepared from photo-chlorination of methylhydropolysiloxanes were hydrolyzed with or without methylchlorosilanes to yield new methylhydroxypolysiloxanes and branched methylpolysiloxanes. Preparation of methylhydrocyclopentasiloxanes was also reported.

*Department of Applied Chemistry*
*Osaka University*
*Miyakojima, Osaka*