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A Convenient Synthesis of α,ω-Difunctionalized Linear Dimethylsiloxanes with Definite Chain Lengths

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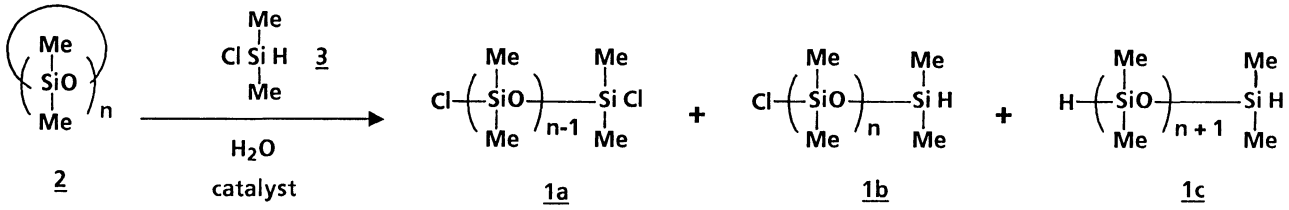
α,ω-Difunctionalized linear dimethylsiloxanes with definite chain lengths are conveniently prepared by the inorganic-solid-catalyzed ring cleavage of cyclodimethylsiloxanes with dimethylchlorosilane and water under very mild conditions.

In contrast to the active investigations in organosilicon chemistry concerning the reactions of silicon-silicon or carbon-silicon linkage, the reactions of organosiloxanes, which are of great industrial importance, have aroused relatively little interest among organic chemists, with the exception of polymerization reactions.[1] The α,ω-difunctionalized linear dimethylsiloxanes with definite chain lengths 1a – 1c have remained to be one of the unexplored silicones because of their troublesome way of preparations.[2] These compounds are key materials for the siloxane block copolymers and silicone resins with strictly ordered structure, which hitherto are unknown in silicone chemistry.

In this communication, we describe a convenient method for the preparation of α,ω-difunctionalized linear dimethylsiloxanes with definite chain lengths 1a – 1c by means of a highly selective ring-cleavage of cyclodimethylsiloxanes 2 using dimethylchlorosilane (3), water and inorganic solids as catalyst (Scheme 1).[3]



Scheme 1.

Frey et al. showed that the reaction between 2 and dimethyldichloro- or methyltrichlorosilane catalyzed by activated carbon at reflux gave ring-cleaved siloxanes of random chain lengths.[4] For the purpose of controlling siloxane chain lengths and selective functionalization of α- and ω-position, we ran the reactions using dimethylchlorosilane 3. A mixture comprising 2, 3 (1.5 – 3.0 equiv.), H_2O (0.001 – 10 equiv.)[5] and the catalyst (1 – 10 wt%)[6] was stirred at room temperature

for 1 – 10 h. The reaction mixture was analyzed on gas chromatography and the products[7] were identified with GC-MS.

Table 1. Effects of the ring size on the ring-cleavage reactions [a]

Entry	2	Reaction time / h	Conversion / % [b]	Yield / % [b]		
				1a	1b	1c
1	D_3 (n=3)	1.0	93.9	5.2	80.3	5.5
2	D_4 (n=4)	4.0	43.0	2.8	25.8	2.5
3	D_5 (n=5)	6.0	7.0	—	6.0	—

a) Reaction conditions : cyclodimethylsiloxanes (10 mmol), dimethylchlorosilane (15 mmol), H_2O (0.19 mmol), activated carbon (Untreated Powder 100 – 400 mesh, Sigma Chemical Company) (0.085 g), room temperature. b) Determined with GLC. Nonane used as an internal standard.

As shown in Table 1, the ring size of 2 strongly affected their conversions to ring-cleaved products. The most strained substrate among 2 , hexamethylcyclotrisiloxane(D_3) 2 (n = 3) was cleaved quantitatively in one hour. The conversions of less strained substrates, such as D_4 2 (n = 4) and D_5 2 (n = 5) were lower than that of D_3, and additional reaction time were not effective to increase their conversions, but promoted redistribution reactions of siloxane chains.

With the above results on hand, we synthesized α-chloro-ω-hydrodimethylsiloxanes 1b from 2 with high selectivity. 1b thus prepared were easily isolable and could be purified by distillation. This is the first reported convenient synthesis of 1b (n = 3 – 5) (Table 2).

Table 2. Selective synthesis of 1b from 2

Entry	2	1b		2
		Isolated yield / %	Purity / % [d]	Recovered / %
1[a]	D_3 (n=3)	73.8	93.0	0
2[b]	D_4 (n=4)	71.3	85.1	64.1
3[c]	D_5 (n=5)	73.6	84.4	74.1

a) D_3 0.45 mol, dimethylchlorosilane 0.68 mol, H_2O 0.052 mol, activated carbon 1.9 g, hexane 100 ml, room temperature 6 h. b) D_4 0.34 mol, dimethylchlorosilane 0.51 mol, H_2O 0.048 mol, activated carbon 2.86 g, room temperature 6.5 h. c) D_5 0.405 mol, dimethylchlorosilane 0.607 mol, H_2O 0.096 mol, activated carbon 4.3 g, room temperature 5 h. d) Purity of 1b was determined with GLC.

In contrast to 1b , selective formation of α,ω-dihydroderivative 1c was accomplished in the presence of equimolar, instead of 10 mol%, amount of water.[8] The best catalyst for this conversion was found to be silicagel (Table 3).

Use of ten times excess of water and silicagel as catalyst increased the selectivity and isolated yield (Table 4). 1c was easily isolated and purified to above 95% only by simple distillation. Similarly as in the case of the runs in Table 1, conversion of 2 decreased with increase in the ring size. However, the selectivities to 1c remain almost constant.

Table 3. Catalysts for ring cleavage of D_4 2 (n = 4) to 1c in the presence of equimolar water [a]

Entry	Catalyst (weight, mg)	Reaction time / h	Conversion % [b]	Selectivity % [b, c]
1	activated carbon [d] (85)	3	72.2	55.0
2	molecular sieves 4A [e] (170)	4	68.7	52.3
3	TiO_2 [e] (85)	3	41.1	65.7
4	SiO_2 [f] (170)	4	40.4	86.1

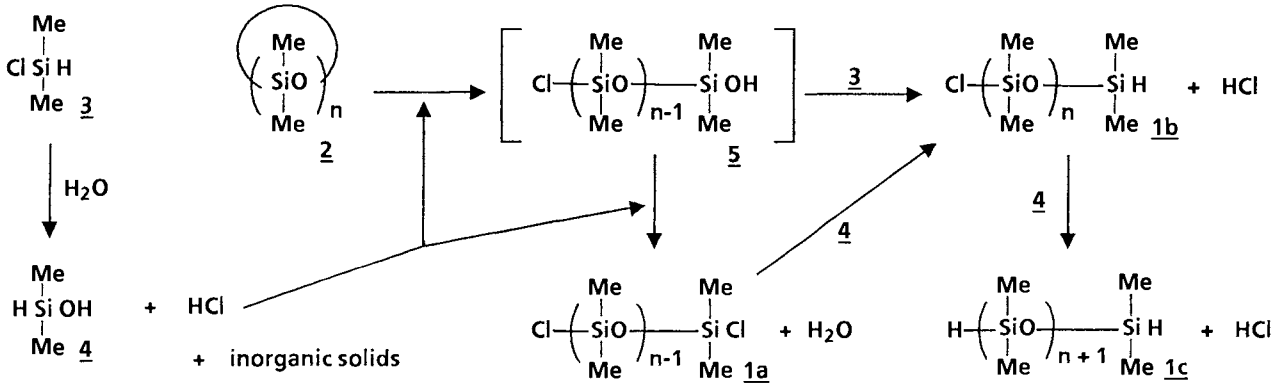
a) The reactions were carried out by D_4 (2.97 g, 10 mmol), dimethylchlorosilane (2.84 g, 30 mmol), catalyst and water (0.18 g, 10 mmol) at room temperature. b) Determined by GLC. c) Defined as 1c / D_4 converted. d) Untreated Powder, Sigma Chemical Company. e) Wako Pure Chemical Industries, Ltd. f) Kieselgel 60, 230–400 mesh, Merck.

Table 4. Synthesis of 1c from 2 [a]

Entry	2	SiO_2 (g) [b]	Conversion % [c]	Selectivity % [c, d]	Isolated yield %
1	D_3 (n=3)	0.1	99.2	94.4	73
2	D_4 (n=4)	0.3	64.2	92.5	78
3	D_5 (n=5)	0.3	37.4	94.1	45
4	D_6 (n=6)	0.3	22.8	99.0	97

a) The reactions were carried out by cyclodimethylsiloxane (10 mmol), dimethylchlorosilane (30 mmol), H_2O (100 mmol), hexane (5 ml, used only in entry 1) and SiO_2 at room temperature with stirring. b) Kieselgel 60, 230–400 mesh, Merck. c) Determined by GLC. d) Defined as 1c / 2 converted.

A possible reaction path is shown in Scheme 2, and further works exploring the reaction mechanisms are continuing. On account of the convenience, mildness and quickness of our reactions, we believe our method offers a great advantage in preparing α,ω-difunctionalized linear dimethylsiloxanes with definite chain lengths, especially on a large scale. These linear dimethylsiloxanes will be utilizable for preparation of either dimethylsiloxane oligomers or siloxane block copolymers with strictly ordered structure, which will find wide application in industry.



Scheme 2.

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3) This method was applied to the synthesis of silicone dendrimers. H.Uchida, Y.Kabe, K.Yoshino, A.Kawamata, T.Tsumuraya, and S.Masamune, J.Am.Chem.Soc., 112, 7077 (1990).

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5) The water content highly influenced both conversion and product ratios. When the water content was less than 1 mol%, the conversion ratio was low. The increase of water content (above 10 mol%) increased the amount of unvolatile materials.

6) Ring-cleavage reactions did not proceed without inorganic solids.

7) All the products were assigned on the basis of the following spectral properties.
1-Chloro-1,1,3,3,5,5,7,7-octamethyltetrasiloxane 1b (n = 3) : bp 39 °C / 0.4 mmHg ; MS m/z 317, 315 (M+ − 1) ; ^{1}H-NMR δ (C_6D_6) 0.13(6H, s), 0.16(6H, s), 0.17(6H, d, J = 2.7 Hz), 0.33(6H, s), 4.94(1H, septet, J = 2.7 Hz) ; ^{29}Si-NMR δ (C_6D_6) − 19.13, − 18.73, − 6.39, 4.00.
1-Chloro-1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane 1b (n = 4) : bp 85 °C / 2 mmHg ; MS m/z 392, 390 (M+ − 1) ; ^{1}H-NMR δ (C_6D_6) 0.15(6H, s), 0.16 − 0.19(18H), 0.34(6H, s), 4.97(1H, broad s) ; ^{29}Si-NMR δ (C_6D_6) − 20.98, − 19.54, − 18.79, − 6.53, 3.92.
1-Chloro-1,1,3,3,5,5,7,7,9,9,11,11-dodecamethylhexasiloxane 1b (n = 5) : bp 82 °C / 0.2 mmHg ; MS m/z 466, 464 (M+ − 1) ; ^{1}H-NMR δ (C_6D_6) 0.15(6H, s), 0.18(24H, broad s), 0.34(6H, s), 4.96(1H, broad s) ; ^{29}Si-NMR δ (C_6D_6) − 21.48, − 21.11, − 19.74, − 18.88, − 6.67, 3.77.
1,1,3,3,5,5,7,7,9,9-Decamethylpentasiloxane 1c (n = 3) : bp 57 °C / 0.5 mmHg ; MS m/z 355 (M+ − 1) ; ^{1}H-NMR δ (C_6D_6) 0.16(18H, s), 0.18(12H, d, J = 3.0 Hz), 4.98(2H, broad s) ; ^{29}Si-NMR δ (C_6D_6) − 21.57, − 19.78, − 6.73.
1,1,3,3,5,5,7,7,9,9,11,11-Dodecamethylhexasiloxane 1c (n = 4) : bp 74 °C / 0.25 mmHg ; MS m/z 429 (M+ − 1) ; ^{1}H-NMR δ (C_6D_6) 0.18(12H, s), 0.19(12H, d, J = 2.7 Hz), 0.21(12H, s), 5.00(2H, septet, J = 2.7 Hz) ; ^{29}Si-NMR δ (C_6D_6) − 21.62, − 19.81, − 6.74.
1,1,3,3,5,5,7,7,9,9,11,11,13,13-Tetradecamethylheptasiloxane 1c (n = 5) : bp 108 °C / 2.0 mmHg ; MS m/z 489 (M+ − 15) ; ^{1}H-NMR δ (C_6D_6) 0.16(12H, s), 0.19(12H, d, J = 2.7 Hz), 0.20(12H, s), 0.21(6H, s), 4.96(2H, septet, J = 2.7 Hz) ; ^{29}Si-NMR δ (C_6D_6) − 21.64, − 19.83, − 6.75.
1,1,3,3,5,5,7,7,9,9,11,11,13,13,15,15-Hexadecamethyloctasiloxane 1c (n = 6) : bp 105 °C / 0.3 mmHg ; MS m/z 563 (M+ − 15) ; ^{1}H-NMR δ (C_6D_6) 0.17(12H, s), 0.19(12H, d, J = 2.8 Hz), 0.21(12H, s), 0.22(12H, s), 4.97(2H, septet, J = 2.8 Hz) ; ^{29}Si-NMR δ (C_6D_6) − 21.60, − 21.58, − 19.76, − 6.68.

8) The decrease of the water (below equimolar) increased the formation of 1a.

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