

REACTIONS OF METHYLHYDROPOLYSILOXANES WITH ACTIVE
CLAY AND CUPRIC OXIDE:
SYNTHESIS OF LOWER MEMBERS OF HYDROGEN
END-BLOCKED DIMETHYLPOLYSILOXANES*

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Many kinds of new methylhydropolysiloxanes containing M' and/or D' units*** have been synthesized by the authors². In the molecules of these compounds there exist two kinds of sites which are easily attacked by ionic reagents, *i.e.* the Si-H and the Si-O bonds, although it is reasonable to assume that these bonds exhibit differences in reactivity. We were interested in investigating reagents which might promote such a difference in reactivity and thus allow a selective reaction. From this viewpoint active clay and cupric oxide were examined.

It is well known that the Si-O-Si linkage is easily cleaved by acids or bases, such as concentrated sulfuric acid or potassium hydroxide, and these reagents have been used widely to prepare silicones by what has been called a rearrangement reaction³ in silicone chemistry. On the other hand, the acids or bases described above are also reactive to Si-H bonds, and therefore they cannot be used for the rearrangement reaction between M'₂ and D₄. Active clay is a very weakly acidic solid of natural origin and belongs to the category of solid Lewis acids. This clay has been found to be useful for the rearrangement of organopolysiloxanes by Ishizuka *et al.*⁴, and thus it was also expected to be useful for this rearrangement. When M'₂ and D₄ were reacted in the presence of active clay below 20°, only linear polysiloxanes were obtained from the product, and as shown in Table 1, most of the hydrogen directly bonded to silicon was retained even after a fairly prolonged period of reaction. It is obvious that the Si-O-Si linkage is more rapidly attacked by active clay than the Si-H bond. From the conditions given in Table 1, hydrogen end-blocked linear dimethylpolysiloxanes, M'D_nM' (*n* = 1-4) were obtained. Properties of these compounds are presented in Table 3. M'D₄M' was obtained by redistillating the residual fraction gathered from

* The NMR spectra of some of these compounds have been discussed previously¹ in relation to the differences in the reactivity of the Si-H bonds in M' and D'.

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*** The short hand notation used here is that which was employed in the preceding paper²:

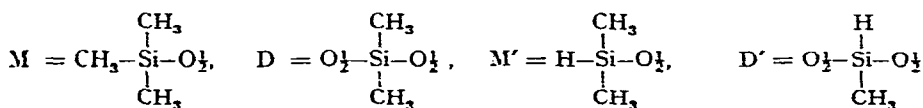


TABLE 1
EQUILIBRATION REACTION OF M'_2 AND D_4 BELOW 20° WITH ACTIVE CLAY^a

Expt. No.	Starting materials			Reaction time in h	Δn_D^{20}	Product %H(Si) found (calcd.) ^b	Residual H(Si) %
	M'_2 mole	D_4 mole	ratio M'/D				
1	0.30	0.08	2	46	0.0049	1.64 (1.92)	88
2	0.22	0.08	1.5	46	0.0036	1.58 (1.68)	94
3	0.25	0.13	1	28	0.0057	1.38 (1.43)	96

^a The amount of active clay is 20% by weight of the polysiloxane mixture. ^b Calculated from the composition of the starting materials.

TABLE 2
THE PERCENTAGE COMPOSITION OF THE PRODUCTS SHOWN IN TABLE 1

Expt. No.	M'_2	$M'DM'$	$M'D_2M'$	$M'D_3M'$	Residue
1	21.7	23.9	19.6	10.9	23.9
2	19.5	21.9	19.5	9.8	29.3
3	11.3	15.1	15.1	13.2	45.3

TABLE 3
PROPERTIES OF LOWER MEMBERS OF HYDROGEN END-BLOCKED DIMETHYLPOLYSILOXANES:
 $H(CH_3)_2SiO[(CH_3)_2SiO]_nSi(CH_3)_2H$

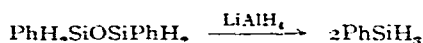
n	Compound	Boiling point $^\circ C/mm$	Refractive index n_D^{20}	Density d_4^{20}	Molar refraction found (calcd.)	%H(Si) found (calcd.)
1	$M'DM'$ ¹	128/760	1.3811	0.8222	58.89 (58.82)	0.95 (0.97)
2	$M'D_2M'$	170-2/760 60/15	1.3883	—	—	0.72 (0.71)
3	$M'D_3M'$	89/15	1.3918	0.8850	95.7 (96.1)	0.57 (0.56)
4	$M'D_4M'$	113/15	1.3938	0.8967	114.8 (114.7)	0.47 (0.47)

each experiment. When the reaction was carried out at *ca.* $40-70^\circ$, the viscosity of the reaction mixture increased rapidly with the evolution of hydrogen, showing that active clay cleaves the Si-H bonds readily at higher temperatures.

If the selective oxidation of M'_2 at the sites of the silicon atoms could be carried out successfully without any side reactions, such as rearrangement of the Si-O-Si

linkages, it would be a very useful method for the synthesis of certain organopolysiloxanes. From this standpoint, it was thought that a metallic oxide might oxidize M'_2 without attacking the Si-O-Si linkage. Cupric oxide reacted appreciably with M'_2 at above 40° , with accompanying evolution of hydrogen gas. From the product $M'DM'$ was isolated. The formation of $M'DM'$ was contrary to expectation because, if no side reaction had been induced, only tetra-, hexa-, or octa-siloxanes would have been obtained. The present result reveals that the rearrangement of the Si-O-Si linkage took place in addition to the oxidation of M'_2 . It was also observed that the mass of cupric oxide which had been reduced as the result of this reaction was found to react exothermally when exposed to air. This indicates that the cupric oxide had been brought into some strongly activated state in the course of the reaction.

It is interesting to clarify the nature of the effective species for the cleavage of the Si-O-Si linkages in this case. The following three chemical species may be considered, namely, (1) metallic copper, (2) unreacted copper oxide and (3) an active copper compound, perhaps involving a hydride of copper, produced by the reduction of cupric oxide. Metallic copper and cupric oxide were found to be ineffective for the equilibration reaction of M_2 and D_4 . Copper mono- and dihydride are known but are so unstable that a separate study of their effect is impractical. However, it may be noted that some metallic hydrides are known to be effective for the cleavage of the Si-O-Si linkage, for example⁵:



In conclusion, it is very probable that the effective species is cupric oxide reduced partially or completely, or copper hydride, either stoichiometric or nonstoichiometric. If the above presumption is correct, continuous oxidation of M'_2 should be possible by reoxidizing a small amount of reduced copper compound by supplying oxygen continuously. In fact, with a catalytic amount of cupric oxide and oxygen gas a considerable amount of $M'D_nM'$ ($n = 1-3$) can be isolated.

1,3,5,7-Tetramethylcyclotetrasiloxane, D'_4 , also contains hydrogen atoms directly bonded to silicon. This compound was, however, not found to react with cupric oxide below 100° with or without a supply of oxygen. When this compound was refluxed with cupric oxide in the presence of oxygen, a pungent gas, probably formaldehyde, was evolved gradually from the reaction mixture, and the sample finally gelled. In this case it is supposed that oxidation at the methyl groups took place giving a three-dimensional high polymer. Thus a definite difference is apparent in the reactivity of cupric oxide toward the Si-H bonds in M'_2 and D'_4 . Methyl-diethylsilane was also examined and found to react easily with cupric oxide.

EXPERIMENTAL

Starting materials

The M'_2 and D_4 used in this study were synthesized from the corresponding methyl (hydro)chlorosilane².

Active clay

Active clay of Mizusawa Chem. Ind. Co. Ltd. was used without further treatment. The result of the analysis of this active clay is as follows: weight loss by heating,

6.43; SiO₂, 72.2; Al₂O₃, 18.41; FeO, 2.08; CaO, 0.18; MgO, 0.298; MnO, 0.019; TiO₂, 0.143; SO₃, 0.25 %.

Rearrangement reaction

To the mixture of M'₂ and D₄ in various mole ratios a small amount of active clay was added. The reaction was carried out at room temperature (10–15°). The refractive index of the reaction mixture was measured several times throughout the reaction. Details of the experiments are presented in Table 1. The oily layer was separated from the clay by filtration and fractionated by a semi-micro Stedman type column of about 50 theoretical plates. The percentage composition of the product is presented in Table 2.

Reaction of M'₂ with cupric oxide

In a 100 cc flask with a reflux condenser, 50 g (0.37 mole) of M'₂ and 3 g (0.038 mole) of cupric oxide was placed. No appreciable reaction was observed at room temperature. When the sample was heated to *ca.* 35–40° the reaction was appreciable with evolution of hydrogen gas from the surface of the cupric oxide. The reaction was exothermic, and no further heating was necessary to continue the reaction. In the last stage of the reaction, the sample was refluxed in order to ascertain the completion of the reaction. The mixture was separated by filtration in air. When the reduced cupric oxide was exposed to air, it glowed with a reddish color and then burned to give a brown-colored mass. A small amount of the filtrate was lost at this stage. The filtrate (43 g) was fractionated by the above mentioned column. From the filtrate, 25 g of M'₂ was recovered. The distillate (12 g) boiling at 128° was found to be M'DM'; *n*_D²⁰ 1.3811 (reported² 1.3811). [Found: H(Si), 0.95. C₆H₂₀O₂Si₃ calcd.: H(Si), 0.97 %.] The residue weighed 6 g.

Continuous oxidation of M'₂ by oxygen with a small amount of cupric oxide

To a flask equipped with a stirrer, an oxygen inlet tube the end of which was placed near the mass of cupric oxide, and a reflux condenser, were placed M'₂ (38 g, 0.5 mole) and cupric oxide (3 g, 0.038 mole). For the first 30 min the reaction was conducted at *ca.* 40°. Thereafter oxygen was blown into the reaction mixture with violent stirring. No heating was necessary owing to the heat of reaction. When the content of the hydrogen directly bonded to the silicon had decreased from 1.50 % to 0.55 %, the reaction was terminated. From the product (27 g), the following polysiloxanes were isolated by fractional distillation: M'₂ (8 g, recovered), M'DM' (3 g), M'D₂M' (7 g), M'D₃M' (6 g) and a higher boiling fraction (3 g).

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SUMMARY

It was found that active clay is applicable to the rearrangement at room temperature between 1,1,3,3-tetramethyldisiloxane, H(CH₃)₂SiOSi(CH₃)₂H, and octamethylcyclotetrasiloxane, [(CH₃)₂SiO]₄, without appreciable fission of the Si–H bonds. Pro-

perties of the rearranged products: hydrogen end-blocked dimethylpolysiloxanes, $\text{H}(\text{CH}_3)_2\text{SiO}[(\text{CH}_3)_2\text{SiO}]_n\text{Si}(\text{CH}_3)_2\text{H}$ ($n = 1-4$), are reported. Cupric oxide reacts with above mentioned disiloxane to give 1,1,3,3,5,5-hexamethyltrisiloxane. In this case, the cleavage of Si-O-Si linkage as well as the expected oxidation of the Si-H bonds took place. The effective chemical species for the rearrangement is not clear; however, it is presumably a kind of hydride of copper.

On the other hand, cupric oxide does not oxidize the Si-H bonds in 1,3,5,7-tetramethylcyclotetrasiloxane, $[\text{H}(\text{CH}_3)\text{SiO}]_4$, but the oxidative cleavage of the methyl groups attached to silicon presumably proceeds in the presence of oxygen at higher temperatures.

The cupric oxide reagent does not activate the rearrangement of hexamethyl-disiloxane and octamethylcyclotetrasiloxane.

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