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Preliminary communication

OXIDATION OF n-DECAMETHYLTETRASILANE WITH PEROXYBENZOIC ACID

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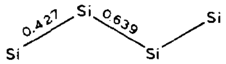
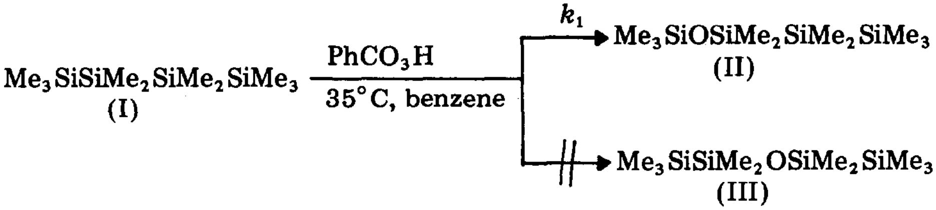
Summary

It is shown, that the first stage of the reaction of n-decamethyltetrasilane with peroxybenzoic acid is oxidation of one of the two terminal Si—Si bonds, rather than oxidation of a central Si—Si bond.

n-Decamethyltetrasilane is the smallest σ-catenate with non-equivalent Si—Si bonds. The central Si—Si bond of $Me_3Si(SiMe_2)_2SiMe_3$ has the highest bond order in the HOMO [1,2], therefore cleavage of this bond by electrophilic reagents is predicted. It is known, for example, that the reaction of permethylated tetrasilane with bromide occurs preferentially at the central Si—Si bond [3] and it is assumed [1], that the interaction of tetrasilane with peracid must proceed analogously. However experimental data for this reaction are unavailable.



We studied the oxidation of n-decamethyltetrasilane by peroxybenzoic acid in benzene at 35° C and found, that in the first stage of the reaction one of the two terminal Si—Si bonds is oxidized, rather than the central bond.



$$\underset{(I)}{Me_3SiSiMe_2SiMe_2SiMe_3} \xrightarrow[35^\circ C,\ benzene]{PhCO_3H} \begin{cases} \xrightarrow{k_1} \underset{(II)}{Me_3SiOSiMe_2SiMe_2SiMe_3} \\ \not\longrightarrow \underset{(III)}{Me_3SiSiMe_2OSiMe_2SiMe_3} \end{cases}$$

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Then, the oxidation of the Si—Si bond adjacent to oxygen occurs:

$$\text{II} \xrightarrow[k_2]{\text{PhCO}_3\text{H}} \underset{\text{(IV)}}{\text{Me}_3\text{SiSiMe}_2\text{OSiMe}_2\text{OSiMe}_3}$$

n-Decamethyltetrasiloxane (VI) is formed in the final stage of the oxidation reaction:

$$\text{IV} \xrightarrow{\text{PhCO}_3\text{H}} \underset{\text{(VI)}}{\text{Me}_3\text{Si(OSiMe}_2)_2\text{OSiMe}_3}$$

n-Decamethyltetrasilane (I) is oxidized more slowly (k_1 0.075 l mol^{-1} min^{-1}) than compound II (k_2 0.15 l mol^{-1} min^{-1}), therefore II is found in a small quantity in the reaction mixture (Fig. 1).

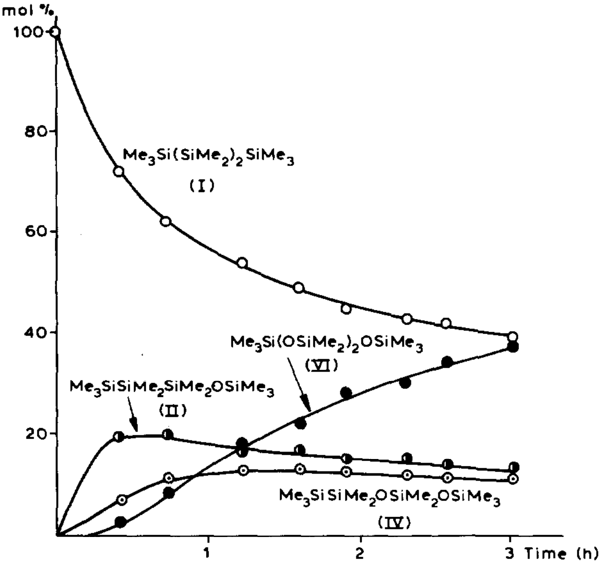

Fig. 1. Kinetic curves of the consumption of substrate and the accumulation of the silicon-containing products in the reaction of decamethyltetrasilane with a double excess of peroxybenzoic acid (benzene, 35° C, $[\text{Si}_4\text{Me}_{10}]_0$ 0.35 mol l^{-1}).

TABLE 1

THE RATE CONSTANTS FOR THE REACTION OF ORGANOSILANES WITH PEROXYBENZOIC ACID AT 35° C IN BENZENE (c_0 0.04—0.07 mol l^{-1})

Compound	Silane	k (l mol^{-1} min^{-1})
I	$\text{Me}_3\text{Si(SiMe}_2)_2\text{SiMe}_3$	0.075
II	$\text{Me}_3\text{SiSiMe}_2\text{SiMe}_2\text{OSiMe}_3$	0.15
III	$\text{Me}_3\text{SiSiMe}_2\text{OSiMe}_2\text{SiMe}_3$	0.34
IV	$\text{Me}_3\text{SiSiMe}_2\text{OSiMe}_2\text{OSiMe}_3$	0.12
V	$\text{Me}_3\text{SiOSiMe}_2\text{SiMe}_2\text{OSiMe}_3$	0.37

The proposed mechanism is supported by kinetic investigations of decamethyltetrasilane oxidation, also by the presence of the four expected intermediates (II—V) (Table 1), and by identification of the products formed. The products are investigated by GLC and by reactions with chlorine.

Interaction of n-decamethyltetrasilane with an equimolar quantity of peroxybenzoic acid in benzene at 20° C, 2 h, gives a mixture from which a fraction (b.p. 87—89° C/15 mmHg) was isolated by distillation. This fraction contains equal quantities of n-decamethyltetrasilane and compound II (or III) as found by GLC (5% "SE30" on Chromatone N-AW-DMCS, 140° C). Upon chlorination of this fraction, Me_3SiCl, Me_2SiCl_2 and $Me_3SiOSiMe_2Cl$ are formed. The latter product may be formed from compound II only.

$$\underset{(I)}{Me_3SiSiMe_2SiMe_2SiMe_3} \xrightarrow{Cl_2} 2\,Me_3SiCl + 2\,Me_2SiCl_2$$

$$\underset{(II)}{Me_3SiOSiMe_2SiMe_2SiMe_3} \xrightarrow{Cl_2} Me_3SiOSiMe_2Cl + Me_3SiCl + Me_2SiCl_2$$

$$Me_3SiSiMe_2OSiMe_2SiMe_3 \xrightarrow{Cl_2} 2\,Me_3SiCl + ClSiMe_2OSiMe_2Cl$$

It may be concluded, that electrophilic attack of peroxybenzoic acid occurs at the terminal Si—Si bond, rather than at the central Si—Si bond, which, may be due to steric effects of the two bulky Me_3Si groups, which shield the central Si—Si bond from reaction with peroxybenzoic acid. Besides this, the statistical factor favours terminal cleavage.

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