A New Oxygen-Insertion Reaction into Silicon-Silicon Bonds with Tertiary Amine Oxides

Hideki SAKURAI, Mitsuo KIRA, and Makoto KUMADA*

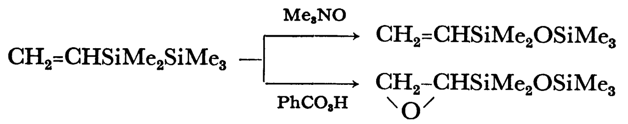
Department of Chemistry, Faculty of Science, Tohoku University, Sendai

**Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto*

(Received December 1, 1970)

We reported an oxidation reaction of organodisilanes with perbenzoic acid.1) Spialter and Austin subsequently described oxidative cleavage of the silicon-silicon bonds with oxides of nitrogen2) and ozone.3) These reagents are regarded as electrophilic and kinetic investigations led to the suggestion of a mechanism similar to that of epoxidation.1,3) We now wish to describe a new and mechanistically interesting insertion reaction of oxygen from tertiary amine oxides into silicon-silicon bonds. The reaction also constitutes a new reduction of amine oxides.4)

Trimethylamine *N*-oxide reacts exothermally with phenoxypentamethyldisilane in dimethyformamide (DMF), yielding phenoxypentamethyldisiloxane in a moderate yield.5) Oxidation of hexamethyldisilane to hexamethyldisiloxane with trimethylamine *N*-oxide required somewhat drastic conditions, the yield being 71% after heating at 90—100°C for 6 hr in DMF. Vinylpentamethyldisilane afforded vinylpentamethyldisiloxane in contrast to the reaction with perbenzoic acid.1)



$$CH_2{=}CHSiMe_2SiMe_3 \xrightarrow{Me_3NO} CH_2{=}CHSiMe_2OSiMe_3$$

$$CH_2{=}CHSiMe_2SiMe_3 \xrightarrow[PhCO_3H]{} \underset{\diagdown O \diagup}{CH_2{-}CH}SiMe_2OSiMe_3$$

Pyridine *N*-oxide reacts more slowly than does trimethylamine *N*-oxide. Treatment of phenoxypentamethyldisilane with pyridine *N*-oxide in DMF, dioxane or toluene afforded phenoxypentamethyldisiloxane in over 85% yield. Although hexamethyl disilane did not react with pyridine *N*-oxide, other organodisilanes such as phenyl, 1,2-diphenyl-, and 1,1-diphenyl-substituted permethylated disilanes gave the corresponding disiloxanes as single products together with pyridine in dioxane.

$$X\text{-}SiMe_2SiMe_3 + C_5H_5NO \longrightarrow X\text{-}SiMe_2OSiMe_3 + C_5H_5N$$

TABLE 1. SECOND ORDER RATE CONSTANTS FOR OXIDATION REACTION OF PHENOXYPENTAMETHYLDISILANES WITH PYRIDINE *N*-OXIDE IN TOLUENE AT 135.0°C[a)]

Substituent	$10^5\,k$,[b)] $l\,mol^{-1}\,sec^{-1}$
p-CH_3O	6.43±0.27
m-CH_3	6.32±0.16
H	9.74±0.50
p-Cl	21.9 ±0.7
m-CF_3	38.7 ±2.4
p-CH_3CO	37.5 ±0.8

a) Initial concentrations of silanes and pyrdine *N*-oxide were 0.02—0.21 mol l^{-1} and 0.03—0.3 mol l^{-1}, respectively.

b) Average of two to four runs.

These results suggest a nucleophilic attack of *N*-oxides on the silicon-silicon bond as a primary step, which was supported by kinetic studies.

The extent of reaction of substituted phenoxypentamethyldisilane with pyridine *N*-oxide in toluene at 135.0°C was followed by the disappearance of disilanes (glpc), the second-order rate law being found to hold accurately. The results are listed in the Table.

A tolerably good Hammett plot was obtained between log (k/k_H) and σ $(r=0.971)$. A positive reaction constant $\rho = +1.18$ indicates nucleophilic attack of *N*-oxides at silicon to be involved in the rate-determining step.

The mechanism and rate parameters of the reaction appeared interesting in connection with the peracid oxidation of disilanes.1)

---

1) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *J. Amer. Chem. Soc.*, **87**, 4001 (1965).

2) L. Spialter and J. D. Austin, *ibid.*, **88**, 1828 (1966).

3) L. Spialter and J. D. Austin, *Inorg. Chem.*, **5**, 1975 (1966).

4) K. Naumann, G. Zon and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788, 7012 (1969), reported the use of hexachlorodisilane as a reducing agent for phosphine oxides, amine oxides, and sulfoxides. They suggested the intermediacy of hexachlorodisiloxane formed by a mechanism involving a free trichlorosilyl anion. In the present study, however, it has been disclosed that organodisilanes are generally capable of reducing amine oxides.

5) Yields of disiloxane depend on the degree of dehydration of $Me_3NO{\cdot}2H_2O$. Main by-products were phenol and $(Me_3SiMe_2Si)_2O$ through hydrolysis.