

## Preliminary communication

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### Silyl anions

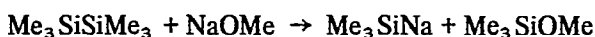
### II\*. A new Si-Si/Si-Si redistribution of hexaalkyldisilanes catalyzed by silyl anions

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(Received December 13th, 1971)

In a previous paper<sup>1</sup>, a facile preparation of trimethylsilylsodium from hexamethyldisilane was described.



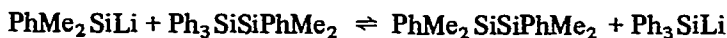
We report here a new Si-Si/Si-Si redistribution reaction found in the course of investigation on trialkylsilyl anions.

As a typical example, *n*-propylpentamethyldisilane (I) was added to a catalytic amount of sodium methoxide (5–10 mole % of I) suspended in hexamethylphosphoramide (HMPA) with stirring under argon, and after 60 sec the mixture was analyzed on VPC. Hexamethyldisilane (II) and 1,2-di-*n*-propyltetramethyldisilane (III) were found in addition to I in an approximately statistical ratio (I/II/III = 2/1/1). In addition to the disilanes, small amounts of disiloxanes were detected. The reaction was reversible, since an equimolar mixture of II and III was synproportionated to I.



These reactions are inhibited by addition of small amounts of substances which react with trimethylsilylsodium, such as anthracene, naphthalene, bromobenzene, and oxygen, which indicates that trialkylsilyl anions are the species responsible for the reaction. This is further evidenced by the fact that the redistribution of I was similarly achieved by a catalytic amount of trimethylsilylsodium prepared separately and free from methoxytrimethylsilane. Representative results are listed in Table 1.

A similar interconversion of phenyl-substituted disilanes with a silyllithium compound are known, for example<sup>2</sup>.



However, a base-catalyzed redistribution of hexaalkyldisilanes is unprecedented. The

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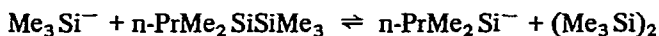
\*For part I, see ref. 1.

TABLE I  
THE Si-Si/Si-Si REDISTRIBUTION OF HEXAALKYLDISILANES

Reactants (mmoles)	Condition	Products (mmoles)
n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (10.0) NaOMe (1.0)	<i>b</i>	(Me <sub>3</sub> Si) <sub>2</sub> (1.9) n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (4.7) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (2.2) siloxanes (1.2)
n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (10.0) NaOMe (0.5)	<i>c</i>	(Me <sub>3</sub> Si) <sub>2</sub> (2.0) n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (4.6) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (2.2) siloxanes (1.2)
(Me <sub>3</sub> Si) <sub>2</sub> (5.0) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (5.0) NaOMe (1.0)	<i>d</i>	(Me <sub>3</sub> Si) <sub>2</sub> (1.9) n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (3.8) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (2.2) siloxanes (2.1)
(Me <sub>3</sub> Si) <sub>2</sub> (5.0) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (5.0) NaOMe (0.5)	<i>c</i>	(Me <sub>3</sub> Si) <sub>2</sub> (2.0) n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (4.3) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (2.3) siloxanes (1.4)
n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (10.0) Me <sub>3</sub> SiNa (1.0) <sup>a</sup>	<i>c</i>	(Me <sub>3</sub> Si) <sub>2</sub> (1.8) n-PrMe <sub>2</sub> SiSiMe <sub>3</sub> (4.3) (n-PrMe <sub>2</sub> Si) <sub>2</sub> (2.1) siloxanes (1.8)

<sup>a</sup> Prepared from Me<sub>3</sub>SiSiMe<sub>3</sub> separately. <sup>b</sup> At room temperature for 2 min. <sup>c</sup> At room temperature for 1 min. <sup>d</sup> At room temperature for 20 sec.

reaction may resemble the related reaction of hexaalkyldigermanes<sup>3</sup> and the mechanism may involve nucleophilic attack of silyl anions on the disilanes, as suggested for the digermanes.



However, it seems desirable to investigate the mechanism further, since the rates of the reaction are unexpectedly rapid for simple nucleophilic substitutions.

Related work on silyl anions is in progress.

#### ACKNOWLEDGMENT

We thank the Tokyo Shibaura Electric Co. for a gift of chlorosilanes.

#### REFERENCES

- 1 H. Sakurai, A. Okada, M. Kira and K. Yonezawa, *Tetrahedron Letters*, (1971) 1511.
- 2 D. Wittenberg and H. Gilman, *Quart. Rev.*, 13 (1959) 116.
- 3 E.J. Bulten and J.G. Noltes, *J. Organometal. Chem.*, 15 (1968) P18.