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TRIMETHYLSILYLSODIUM. A NEW PREPARATION AND SOME REACTIONS INVOLVING A FACILE ELECTRON TRANSFER FROM TRIMETHYLSILYL ANION TO NAPHTHALENE

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During the course of an investigation on oxidation of organodisilanes with perbenzoic acid (1) and with tertiary amine N-oxides (2) we have found that trimethylsilylsodium (I) can be prepared very conveniently from hexamethyldisilane by a reaction with sodium methoxide in hexamethylphosphoramide (HMPA). Triorganosilyl-alkali metal compounds having at least one phenyl group on a silicon atom can be prepared by the Gilman's procedure (3) in which silicon-silicon bonds of hexaorganodisilanes are cleaved with alkali metals in tetrahydrofuran.

$$2PhR_2SiCl \xrightarrow{2M} PhR_2SiSiR_2Ph \xrightarrow{2M} 2PhR_2SiM$$

M = Li, K
  Na (with electron transport agents such as naphthalene)
R = Ph or Me

However, hexaalkyldisilanes are quite inert toward metal cleavage and hence this method can not be applied to the preparation of trialkylsilyl-alkali metal compounds (4). Only recently, Vyazankin et al., (5) and Hengge and Holtschmidt (6) have been successful in the preparation of trialkylsilyllithium from bis(trialkylsilyl)mercury by a metal-metal exchange reaction. However, the method required bis(trialkylsilyl)mercury as a starting material and appeared rather tedious as compared with the present method.

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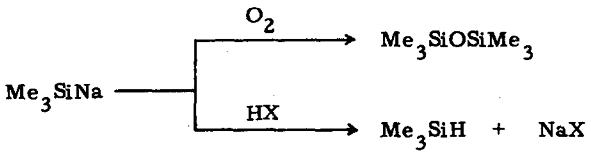
To a stirred suspension of dry sodium methoxide in HMPA was added slowly an equimolar amount of hexamethyldisilane. The sodium methoxide began to dissolve immediately and a clear reddish brown solution of I was obtained instantaneously in laboratory time scale. Trimethylmethoxysilane can be removed from the solution under reduced pressure. The solution was very sensitive toward air and protic solvents yielding hexamethyldisiloxane and trimethylsilane respectively, but it can be stored under inert atmosphere for several days at room temperature. The driving force of the present reaction to give I is apparently the formation of a silicon-oxygen bond since treatment of hexamethyldisilane with sodium in HMPA did not yield I.

$$Me_3SiSiMe_3 \quad + \quad NaOMe \xrightarrow{HMPA} Me_3SiNa\,(I) \quad + \quad Me_3SiOMe$$



$$Me_3SiNa \xrightarrow{O_2} Me_3SiOSiMe_3$$

$$Me_3SiNa \xrightarrow{HX} Me_3SiH \quad + \quad NaX$$

Reactions of I with various substrate, especially with organic halides, were examined. The product from the reaction of I with an equimolar amount of either bromobenzene or chlorobenzene was phenyltrimethylsilane, formed in 44 - 57% and 30% yields, respectively. No biphenyl was detected. Reaction of I with an equimolar amount of benzyl chloride gave benzyltrimethylsilane (18%) and bibenzyl (47%) in addition to hexamethyldisiloxane. Alkyl halides also gave substitution products and reductive dimers, the relative yields depending upon the nature of halogens. Thus, formations of the reductive dimers are characteristic features of these reactions. Representative results on n-butyl halides are listed in TABLE. However, it is of interest to note that a reaction of I with an equimolar quantity of neopentyl bromide proceeded very readily to give only neopentyltrimethylsilane in 49% yield; no reductive dimer was formed.

Now these results suggest that the reaction may involve an electron transfer from I to substrates to yield alkyl and silyl free radicals as an initial process rather than a simple bimolecular nucleophilic reaction, although discussion of the detailed mechanism requires further research.

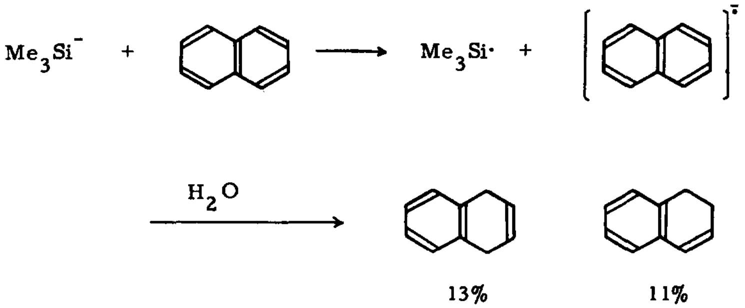
However, we have observed an important solid evidence that demonstrates such a facile electron transfer taking place actually from I to certain substrates such as naphthalene. Thus, addition of equivalent amount of naphthalene to a solution of I followed by hydrolysis gave 1, 2- and 1, 4-dihydronaphthalene.

TABLE

Product Distribution from the Reaction of Trimethylsilylsodium with n-Butyl Halides

Halogen	Temp (°C)	Yield (%)		Molar ratio of
		n-BuSiMe$_3$	(n-Bu)$_2$	(n-Bu)$_2$/ n-BuSiMe$_3$
Cl	ambient	20.2	0.7	0.017
	ambient[a]	18.2	0.9	0.024
Br	10	32.9	10.9	0.17
I	ambient	33.8	11.9	0.18

a : Trimethylsilylsodium was prepared in the presence of alkyl halides (*in situ* method).



The existence of the intermediate naphthalene anion radical was verified by its esr spectra ; twenty five line spectrum is in accord with the reported spectra of the anion radical (7). The hyperfine constants and assignments are :

$$a^{H}_{1,4,5,8} = 4.84 \; ; \qquad a^{H}_{2,3,6,7} = 1.79 \text{ gauss.}$$

Trimethylsilylsodium is promising as a reagent in synthetic organosilicon chemistry as well as an electron transfer reagent. Further studies are in progress.

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