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The Reaction of Organodisilanes with *N*-Bromosuccinimide[1]

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The reactions of three hexaorganodisilanes with *N*-bromosuccinimide in carbon tetrachloride or in chloroform were carried out. Hexamethyldisilane afforded trimethylbromosilane (82.9—100%) and *N*-trimethylsilylsuccinimide (73.5—79.5%). No bromomethylpentamethyldisilane was obtained. Similarly, 1, 2-diphenyltetramethyldisilane gave phenyldimethylbromosilane and a small amount of bromobenzene. The *N*-silyl compound could not be isolated, but succinimide was obtained as a decomposition product. Phenylpentamethyldisilane gave trimethylbromosilane and phenyldimethylbromosilane in 67.4 and 12.3% yields respectively. A possible reaction mechanism was discussed.

N-Bromosuccinimide (NBS) is known as an efficient brominating agent, especially for allylic carbons;[2] it may react via a free radical chain mechanism in non-hydroxylic solvents.

Since the introduction of a halogen into a methyl group of hexamethyldisilane or other related compounds is a highly desirable operation in the field of organosilicon chemistry, we have investigated the reaction of hexamethyldisilane with NBS, primarily in the hope of preparing (bromomethyl)-pentamethyldisilane. However, contrary to our expectation, the reaction led to a cleavage of the silicon-silicon bond, even in non-polar solvents. In view of these findings, it became of interest to investigate the reaction for variously substituted disilanes, since NBS is known to react as a positive halogen donor to an olefin only in polar protic solvents.[3]

While the present work was in progress, Calas, Frainnet and Dentone[4] have also briefly described the formation of methyldiethylbromosilane and *N*-methyldiethylsilylsuccinimide by the reaction of 1, 2-dimethyltetraethyldisilane with NBS.

In the present paper, we wish to report some of our own results especially from the mechanistic point of view.

Results and Discussion

The reaction of the three organodisilanes employed here with NBS leads to the cleavage reaction, giving bromosilanes and *N*-silylsuccinimides instead of (bromomethyl)disilanes. The results are summarized in Table I. It is interesting to note that trimethylbromosilane was a major product in the reaction of phenylpentamethyldisilane with NBS.

NBS has been considered to undergo a reaction in which the initial attack on the substrate in the bromination is possibly by the succinimido radical and in which the chain-propagating step is the attack on the second NBS molecule by the resulting carbon radical.[5]

Hydrogen atoms of hexamethyldisilane have been

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1) Preliminary experiments were cited in M. Kumada and R. Okawara, "Yukikeiso Kagaku (Organosilicon Chemistry)," Maki, Tokyo (1959), p. 74.

2) C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

3) L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

4) R. Calas, E. Frainnet and Y. Dentone, *Compt. rend.*, **259**, 3777 (1964).

5) C. Walling, "Free Radicals in Solutions," John Wiley & Sons, New York (1957).

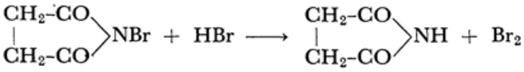
TABLE I. THE REACTION OF ORGANODISILANES WITH N-BROMOSUCCINIMIDE[a]

Disilanes	Solvent	Product	(% yield)
$(CH_3)_3SiSi(CH_3)_3$	$CHCl_3$	$(CH_3)_3SiN(COCH_2)_2$	(79.5)
		$(CH_3)_3SiBr$[b]	(82.9)
$(CH_3)_3SiSi(CH_3)_3$	CCl_4	$(CH_3)_3SiN(COCH_2)_2$	(73.5)
		$(CH_3)_3SiBr$[b]	(100)
$C_6H_5(CH_3)_2SiSi(CH_3)_3$	CCl_4	$(CH_3)_3SiBr$[b]	(67.4)
		$C_6H_5(CH_3)_2SiBr$[b]	(12.3)
		C_6H_5Br, small amount	
		$(CH_2CO)_2NH$[c]	(77.1)
$C_6H_5(CH_3)_2SiSi(CH_3)_2C_6H_5$	CCl_4	$C_6H_5(CH_3)_2SiBr$[b]	(76.6)
		C_6H_5Br, small amount	
		$(CH_2CO)_2NH$[c]	(67.7)

a) Equimolar amount of NBS to disilanes was employed.
b) Determined by titration.
c) Possibly, decomposition compound of $C_6H_5(CH_3)_2SiN(COCH_2)_2$.

shown to be abstracted by a number of electron-seeking radicals, such as benzoyloxy,[6] t-butoxy[7] and trichloromethyl[7] radicals. Therefore, it may be expected that hexamethyldisilane can be brominated by chain reactions involving homolytic hydrogen abstraction by succinimido radicals in non-polar solvents. Accordingly, the reaction of hexamethyldisilane with NBS does not involve this sort of free-radical-chain mechanism.

Alternatively, recent evidence[8,9] indicates that the mechanism of NBS bromination may actually involve bromine molecules rather than NBS as the chain-carrying species; namely, NBS may function only by producing bromine molecules at a low concentration:

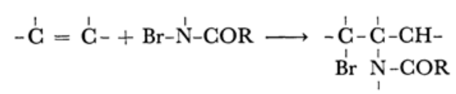


$$Br_2 \rightleftharpoons 2Br\cdot$$

$$Br\cdot + RH \longrightarrow HBr + R\cdot$$

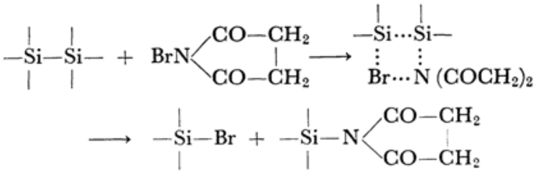
If this is the case, the cleavage of the silicon-silicon bond may be expected, since hexaalkyldisilanes are considerably reactive towards bromine molecules.[10] In fact, immediately after a first portion of hexamethyldisilane had been added to a cold suspension of NBS, a red color of bromine developed throughout the reaction. Moreover, the fact that diphenyltetramethyldisilane requires a higher temperature to complete the reaction may indicate that some sort of electrophilic attack on the silicon-silicon bond occurs.[10]

However, such a mechanism is not sufficient to account for the formation of N-silylsuccinimides. The simplest mechanism consistent with the facts seems to be one in which an intermediate of a four-center type is involved. In general, the silicon-silicon bond undergoes a variety of electrophilic and oxidative cleavage reactions. Many examples suggest that the cleavage reactions may resemble the corresponding electrophilic addition reactions to the carbon-carbon double bond.[11] N-Bromoamides are also known to have a tendency to form an addition compound with a carbon-carbon double bond; some of these addition compounds have been isolated.[2]



$$-\overset{|}{C}=\overset{|}{C}- + Br-\overset{|}{N}-COR \longrightarrow -\overset{|}{\underset{Br}{C}}-\overset{|}{\underset{\underset{|}{N}-COR}{C}}-CH-$$

Therefore, although the possibility of a mechanism involving molecular bromine can not be excluded, the product distribution in the reaction of phenylpentamethyldisilane with NBS suggests that the probable mechanism for this reaction is the direct attack of NBS on the silicon-silicon bond through a four-center transition state. Such a process must be likely in carbon tetrachloride or chloroform, since the solvents have no nucleophilic power and since no separation of ions, which is improbable in a weakly polar reaction, is necessary.



The bromine atom may orient to the more negative silicon atom, so that trimethylbromosilane is formed as a major product in the reaction of phenylpentamethyldisilane with NBS.

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Experimental

Materials.—NBS,[12] hexamethyldisilane,[13] phenylpentamethyldisilane,[14] and 1, 2-diphenyltetramethyldisilane[15] were prepared by the reported procedure.

The Reaction of Hexamethyldisilane with NBS in Chloroform.—To a stirred and externally-cooled suspension of 37.5 g. (0.21 mol.) of NBS in 50 ml. of dry chloroform, there was added, drop by drop, 34 g. (0.23 mol.) of hexamethyldisilane. Immediately after a first portion of hexamethyldisilane had been added, the red color of bromine developed. After the addition had been completed, the solution was stirred at room temperature for 1 hr., then an almost complete decolorization occurred. The mixture was then submitted to distillation to give the following fractions: (a) chloroform and trimethylbromosilane, boiling up to 80°C (110 g.); and (b) fraction boiling at 120°C (18 mmHg) (27 g.). The redistillation of Fraction a through a 35 cm. column packed with glass helicoils gave 31 g. of trimethylbromosilane, b. p. 80°C, contaminated with a small amount of chloroform. The mixture was analyzed by titrating the hydrolyzable bromine and so estimated to contain 26.8 g. (0.175 mol., 82.9%) of trimethylbromosilane. Fraction b was quite hygroscopic and decomposed to succinimide, m. p. 123—125°C, and hexamethyl disiloxane upon treatment with water. The redistillation of Fraction b gave pure *N*-trimethylsilylsuccinimide, n_D^{20} 1.4732, d_4^{20} 1.0684, MR_D 44.99 (calcd. 45.18).

Found: Si, 16.7. Calcd. for $C_7H_{13}O_2NSi$: Si, 16.4%.

The Reaction of Hexamethyldisilane with NBS in Carbon Tetrachloride.—To a stirred suspension of 37.5 g. (0.21 mol.) of NBS in 50 ml. of dry carbon tetrachloride, 31 g. of hexamethyldisilane was added in virtually the manner described above. After work-up, *N*-trimethylsilylsuccinimide (25 g., 73.5%) and trimethylbromosilane (33.7 g., 100% by titration) were obtained.

The Reaction of 1, 2-diphenyltetramethyldisilane with NBS in Carbon Tetrachloride.—1, 2-Diphenyltetramethyldisilane (20 g., 0.074 mol.) in 100 ml. of dry carbon tetrachloride was added to a stirred suspension of 13 g. of NBS (0.073 mol.) in 30 ml. of carbon tetrachloride. External heating was necessary to keep the reaction proceeding. After the addition was complete, the reaction mixture was submitted to distillation. After the carbon tetrachloride has been removed, b. p. 75°C, a fraction boiling at 118—125°C (50 mmHg) (12.5 g.) was obtained. The gas chromatographical analysis of the fraction indicated the presence of phenyldimethylbromosilane (main component) and bromobenzene. The amount of phenyldimethylbromosilane was determined by titration to be 12.0 g. (yield 76.6%). The distillation residue, possibly *N*-phenyldimethylsilylsuccinimide, could not be distilled off successfully, but 4.9 g. (67.7%) of succinimide was obtained as a decomposition product, b. p. 148°C (2 mmHg).

The Reaction of Phenylpentamethyldisilane with NBS in Carbon Tetrachloride.—Phenylpentamethyldisilane (15 g., 0.072 mol.) was allowed to react with NBS (13 g., 0.073 mol.) in carbon tetrachloride in the same manner. Moderate heating was necessary to initiate the reaction. After work-up as described above, 74 g. of a mixture of carbon tetrachloride and trimethylbromosilane, b. p. 75—78°C, 3 g. of a mixture of phenyldimethylbromosilane and bromobenzene, 63°C (31 mmHg), and 5.5 g. (77.1%) of succinimide were obtained. The amounts of trimethylbromosilane and phenyldimethylbromosilane were determined by titration to be 7.4 g. (67.4%) and 1.9 g. (12.3%) respectively.

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