oxides which result render the procedure hazardous and difficult to monitor.

In this Laboratory it has been found convenient to dispose of small (*e.g.*, 100 g.) quantities of chlorine trifluoride by passing the gas through a stainless steel trap filled with silicon metal. Low pressures of chlorine trifluoride react quite readily with silicon to form the very stable silicon tetrafluoride and chlorine. These can be collected in a liquid nitrogen trap and disposed of rather easily. A silicon trap also can be used for BrF_3 disposal.

The trap used in this Laboratory was designed for 1 mole of chlorine trifluoride and consisted of a 10-in. length of 1.5-in. (o.d.), $^1/_8$-in. walled stainless steel (Type N) tubing with a lid of 0.25-in. stainless steel plate. The trap was connected to the reaction system by a 0.25-in. stainless steel Swagelok[3] coupling with Teflon ferrules. The parts of the trap were silver soldered together and the lid was held on with six screws. A 60-mil Teflon gasket was machined to match the collar and several concentric grooves were cut in the lid and collar to help assure a vacuum-tight fit when the lid was in place. The trap was filled with crushed silicon, obtained by breaking silicon lumps with a hammer. It was found advisable to avoid loading the trap with silicon dust any finer than 100–150 mesh, as it tended to be blown through the lines and into the vacuum pump.

The main precaution to be observed when using this trap is to avoid passing ClF_3 into it too rapidly as the reaction is quite exothermic. When chlorine trifluoride at 1 atm. pressure was passed through the trap for 30 sec., the bottom three inches of the trap became orange hot (~750°). This could harm the silver-soldered connections if it continued very long.

This disposal system offers these advantages: (1) simply rattling the trap tells one how much silicon there is remaining, (2) the reaction products are safely collected in a cold trap and are conveniently released by letting the cold trap warm up slowly in a hood and bubbling the Cl_2 and SiF_4 vapors through aqueous base for hydrolysis, and (3) there is less danger of getting hazardous gases into the vacuum pump or into the room and no risk of explosions.

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The Reaction of Silicon Tetrachloride with N,N-Dimethylhydrazine and Hydrazine

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The formation of compounds containing silicon–nitrogen bonds by the reaction of organohalosilanes with hydrazine and some of its alkyl-substituted derivatives has been given recent attention.[2–6] Compounds of the general types monotriorganosilyl-,[2,5] bis-(N,N′-triorganosilyl)-,[2,5] bis-(N,N-triorganosilyl)-,[2] and tris-(triorganosilyl)-hydrazine have been prepared in large number and their properties described. Tetrasilylhydrazine, $(H_3Si)_2NN(SiH_3)_2$, also has been prepared.[4] All of these compounds were prepared from a triorganohalosilane and the appropriate hydrazine. Reaction of hydrazines with diorganodihalosilanes[3,6] in dilute solution leads to the formation of six-membered ring compounds containing the $[-Si-N-N-]_2$ core with various alkyl or aryl groups as well as hydrogen atoms as substituents. However, the reaction of hydrazine, N_2H_4, and $(CH_3)_2SiCl_2$, which is of this type, led to the formation of a polymeric substance which analyzed for $[-Si(CH_3)_2-NHNH-]_x$ and possessed a molecular weight of about 3500.[2]

A general review of the field of silicon–nitrogen compounds was given recently by Fessenden and Fessenden.[7]

The purpose of the present investigation was to see if well defined compounds were formed in the reaction of even more highly halogenated silanes (in particular, $SiCl_4$) and various hydrazines. We hoped to prepare compounds containing four nitrogen atoms bonded to silicon in contrast to the known silicon–hydrazine compounds in which at most two nitrogen atoms per silicon had been obtained.

Under strictly anhydrous conditions and in the presence of an inert atmosphere, the reaction of a CCl_4 solution of silicon tetrachloride ($SiCl_4$) and an excess of N,N-dimethylhydrazine, $(CH_3)_2NNH_2$, proceeds smoothly with the formation of tetra-(N,N-dimethylhydrazino)-silane, $Si[-NHN(CH_3)_2]_4$, and the by-product N,N-dimethylhydrazine hydrochloride, $(CH_3)_2NNH_2{\cdot}HCl$, according to the reaction

$$SiCl_4 + 8(CH_3)_2NNH_2 = Si[-NHN(CH_3)_2]_4 + 4(CH_3)_2NNH_2{\cdot}HCl$$

The reaction is exothermic and proceeds by a mechanism[2,8] involving the elimination of HCl. The HCl so formed reacts with excess hydrazine to give the hydrochloride.

$Si[-NHN(CH_3)_2]_4$ is a white, crystalline solid, stable for several weeks in a sealed tube at room temperature, but is very sensitive to traces of moisture, hydrolyzing to give the hydrazine and, presumably, various silicic acids. It possesses a relatively low m.p. of 64°. The infrared and n.m.r. spectra of this material are consistent with the above formulation.

(1) (a) To whom requests for reprints should be sent. (b) Based, in part, on the research work undertaken by J. R. C., in partial fulfillment of the requirements for the Ph.D. Degree at the Illinois Institute of Technology.

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Mention should be made of an attempt to isolate a well defined compound from a similar reaction of $SiCl_4$ and the parent hydrazine, N_2H_4. In this instance, the silicon-containing compound as well as the hydrazine hydrochloride was insoluble in the organic solvent (C_6H_6 or CCl_4). Repeated washing of the insoluble product from this reaction with N_2H_4 removed the soluble $N_2H_4 \cdot HCl$[9] leaving behind a white residue which analyzed as $SiCl_{0.8}(N_2H_4)_{2.9}$. This material was very susceptible to hydrolysis and proved to be insoluble in the common organic solvents. The product was attacked, however, by hydroxy-containing solvents, resulting in cleavage of the Si–N bonds. On the basis of these observations, it is suggested that the product of this reaction is polymeric in nature, in contrast to the compound obtained from the $SiCl_4$–$(CH_3)_2NNH_2$ reaction. This is not unreasonable in view of the fact that the N_2H_4 has reaction sites on both nitrogen atoms while the presence of methyl groups in $(CH_3)_2NNH_2$ prevents reaction from occurring on the methyl-substituted nitrogen atom.

Because of its insolubility, no further information was obtained about the product from the $SiCl_4$–N_2H_4 reaction. In short, no evidence of any well defined compound from the reaction of these two compounds was obtained.

Experimental

Apparatus.—Because of the necessity for eliminating moisture (and probably oxygen) from the reactions involving $SiCl_4$ and any of the hydrazines, the apparatus shown in Fig. 1 was devised. A is a modified 500-ml. 3-necked flask which is joined by means of a 45° adapter (B) to a 500-ml. reaction flask, C. Connecting C with the receiving flask F is tube D with its fritted disk E positioned so that it is at the bottom of C in the illustrated arrangement. F, the receiver, possesses numerous side arms (not shown in detail) which can be removed with product samples. The center neck of A leads to a vacuum pump and a dry nitrogen supply by means of a stopcock. The remaining two necks of A are fitted with Teflon-stoppered burets containing the reaction solutions. Elsewhere, all stopcocks and joints are of glass sealed with Dow Corning high vacuum silicone grease.

During the course of a reaction, flask C was in a position 180° clockwise from that shown in Fig. 1, having been rotated about the joint connecting it with B. In this position, the fritted disk, E, was well above the reacting solution in C. This prevented any precipitate formed in a reaction from clogging the disk. The reactions were carried out under an atmosphere of dry nitrogen; the system then was evacuated and the flask C rotated to the position shown in Fig. 1. Dry N_2 then was admitted to the system, causing liquid in C to be forced into the evacuated receiver, F, through the filter E. This proved to be an effective means of filtration without exposing the products to the atmosphere. Receiver F then was sealed off at some convenient point along D. Samples of product solution then were poured into the various side arms of F. If, for a given sample, the solvent was not desired, the receiver could be reattached to the vacuum line at G and the solvent removed. It is felt that this method of treatment of the products of the reactions described was necessary and sufficient to protect them from moisture and atmospheric oxygen.

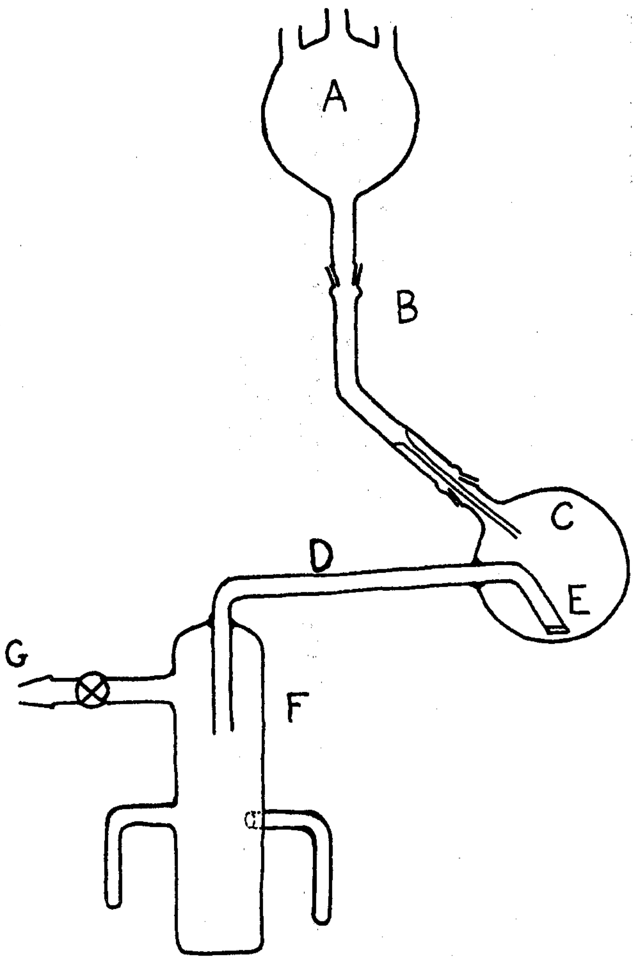

Fig. 1.—Schematic diagram of the apparatus used in the preparation of $Si[-NHN(CH_3)_2]_4$.

Reagents.–N,N-Dimethylhydrazine (anhydrous, 98–99%, from Matheson, Coleman and Bell, Inc.), which had been refluxed *in vacuo* at 50–60° for 1 hr. with five times its weight of crushed BaO (in order to remove the last traces of moisture) and then distilled, analyzed as 100 wt. % $(CH_3)_2NNH_2$ both by potentiometric titration of its acid salt and by oxidation with saturated KIO_3 in the presence of excess HCl using wool red 40F internal indicator.[10,11]

$SiCl_4$ (99.8% from Matheson Coleman and Bell, Inc.) was prepared for use by simple distillation in which the first and last portions of distillate were rejected. An equal volume of CCl_4 (Analytical Reagent from Mallinckrodt) previously dried over P_2O_5 was distilled into the $SiCl_4$. The solution was analyzed gravimetrically for silicon and chloride using well established procedures.[12]

N_2H_4 (anhydrous, 95+% from Matheson Coleman and Bell, Inc.) was purified by double distillation from crushed BaO.[13] The sample to be purified was refluxed *in vacuo* with five times its weight of BaO at 70° and distilled. The process was repeated with one half the original amount of BaO. The material so obtained analyzed as 100 wt. % N_2H_4 by oxidimetric titration with saturated KIO_3.[11]

Preparation of Tetra-(N,N-dimethylhydrazino)-silane.—To 100 ml. of freshly distilled CCl_4 in flask C of Fig. 1 was added 10.0 ml. of 4.14 *M* $SiCl_4$ in CCl_4 (0.0414 mole). With magnetic stirring, 30.0 ml. of $(CH_3)_2NNH_2$ (0.396 mole) was added slowly over a period of 1 hr. Upon complete addition, the solution was filtered, the insoluble $(CH_3)_2NNH_2 \cdot HCl$ remaining in C. The filtrate was collected in receiver F and isolated from the system by

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(9) The solubility of $N_2H_4 \cdot HCl$ was found to be 1.4 g./ml. of N_2H_4 at 25.0 ± 0.1°.

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sealing off along D. Following solvent removal through G, a white, crystalline material with m.p. 63.4–64.2° remained.

A hydrolyzed sample was analyzed for Si and $(CH_3)_2NNH_2$. *Anal.* Calcd. for $Si[-NHN(CH_3)_2]_4$: Si, 10.62; $(CH_3)_2NNH-$, 89.38. Found (separate preparations): Si, 10.78, 10.50, 10.59; $(CH_3)_2NNH-$, 88.13, 88.80, 91.65. The yield from a typical preparation was 80% based on the amount of $SiCl_4$ taken.

Molecular Weight.—The molecular weight of $Si[-NHN(CH_3)_2]_4$ was determined by the method of freezing point depression in C_6H_{12} (Spectroquality from Fisher Scientific Co.). Calcd. for $Si[-NHN(CH_3)_2]_4$: 264. Found (separate preparations): 277, 264.

Infrared Spectra.—The infrared spectrum of a CCl_4 solution of $Si[-NHN(CH_3)_2]_4$ is similar to that of the parent hydrazine. The spectrum of a sample of $(CH_3)_2NNH_2$ used in the preparation of the product was equivalent in detail to that reported by Shull and co-workers[14] and to that of Pierson and co-workers.[15] A comparison of the spectrum of $(CH_3)_2NNH_2$ and $Si[-NHN(CH_3)_2]_4$ revealed the following (all assignments are due to Shull).[14]

(1) The strong N–H stretching doublet in the 3200 cm.$^{-1}$ region of the hydrazine spectrum appeared as a medium intensity singlet near 3300 cm.$^{-1}$ in the product spectrum. Also, a strong N–H deformation band at 1595 cm.$^{-1}$ in the $(CH_3)_2NNH_2$ spectrum was absent in that of $Si[-NHN(CH_3)_2]_4$. Both of these observations are characteristic of a change from an $-NH_2$ functional group to an $-NH$ group.[16]

(2) The spectrum of the product exhibited new absorptions at 2999 (m), 1386 (s), and 1233 (m–s) cm.$^{-1}$ but it was missing an absorption at 1308 (m) cm.$^{-1}$ found in the hydrazine. Presumably, these new absorptions are characteristic of the silicon–nitrogen bond.

(3) A very strong absorption at 1054 cm.$^{-1}$ in the $(CH_3)_2NNH_2$ spectrum apparently had shifted to 1072 cm.$^{-1}$ in the $Si[-NHN(CH_3)_2]_4$ spectrum, and a strong singlet in the 900 cm.$^{-1}$ region appeared as a doublet, very strong in intensity centered at 890 cm.$^{-1}$ in the product spectrum.

All infrared spectra were taken on a Perkin-Elmer Model 21 recording infrared spectrophotometer utilizing NaCl optics. The sample of $Si[-NHN(CH_3)_2]_4$ was a 0.31 *M* solution in CCl_4. The sample of $(CH_3)_2NNH_2$ was a 3.3 *M* solution also in CCl_4. Both samples were prepared and placed in the infrared cells in a drybox under an atmosphere of nitrogen. The cells used were the conventional solution cells with NaCl windows and a path length of 0.1 mm. The uncertainty in the absorption frequencies reported above is ±2 cm.$^{-1}$ except for very broad bands in which the uncertainty is greater.

Proton Magnetic Resonance Spectra.—The proton magnetic resonance spectrum of $Si[-NHN(CH_3)_2]_4$ (approximately 1 *M* in CCl_4) consisted of two signals. The absorption due to the methyl protons was a single sharp signal with a τ (tau) value[17] of 7.67. The signal due to the NH proton was very broad (width at half height was approximately 0.12 p.p.m.) with $\tau = 7.81$. The total area under the peak representing the NH proton was one sixth of the area due to the methyl protons as would be expected.

It is interesting to note that the proton magnetic resonance spectrum of pure trimethylhydrazine, $(CH_3)_2NNHCH_3$, which in some ways presents an environment to the $(CH_3)_2N-$ and $=NH$ groups similar to that of the product, gives τ values for these protons quite similar to those of the product. These values are: $(CH_3)_2N-$, $\tau = 7.64$; $=NH$, $\tau = 7.75$ (and $CH_3N=$, $\tau = 7.52$). Here again, the $=NH$ signal is very broad having a width at half height of about 0.07 p.p.m.

All of the above spectra were taken on a Varian Model A-60 analytical n.m.r. spectrometer. Chemical shifts were determined using the side-band technique developed by Arnold and Packard,[18] and the values reported are accurate to within ±0.01 unit.

Reaction of Anhydrous Hydrazine and Silicon Tetrachloride.—Because both the silicon-containing product and the hydrazine hydrochloride formed in the reaction of anhydrous N_2H_4 and $SiCl_4$ were insoluble in the solvents used (C_6H_6 or CCl_4), there was no necessity for the filtering device shown in Fig. 1. The reaction was carried out in a 500-ml. round bottom three-necked flask fitted with burets for dispensing the reactants and the center neck connected through a stopcock to a source of vacuum and dry nitrogen.

In a typical reaction, 21.0 ml. of anhydrous N_2H_4 (0.655 mole) was added slowly over a period of 0.5–1 hr. to a solution containing 150 ml. of sodium-dried C_6H_6 and 10.6 ml. of a C_6H_6 solution 3.4 *M* in $SiCl_4$ (0.366 mole). The mixture was held at room temperature throughout the reaction. Upon complete addition, the reaction mixture was transferred to a drybox and filtered. The insoluble material was washed three times with 10–15-ml. portions of anhydrous N_2H_4 and twice with 10–15-ml. portions of sodium-dried C_6H_6. The washed product was dried *in vacuo* for 10 hr., ground to a fine powder, and the drying process was continued for another 5 hr.

Anal. Found (separate preparations): Si, 17.72, 17.85, 18.44; Cl, 17.44, 20.35, 19.51; N_2H_3-, 58.67, 56.61, 58.92. Empirical formula based on the above analyses: $SiCl_{0.84\pm0.06}(N_2H_3-)_{2.92\pm0.05}$.

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