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15. SILICA GEL (CORRECTION)[1]

$$Na_2O\cdot xSiO_2 + H_2SO_4 \rightarrow Na_2SO_4 + xSiO_2 + H_2O$$

Submitted by Robert F. Ruthruff*
Checked by H. S. Booth† and Albert Dolance†

Mr. William S. Heinaman‡ has called attention to the fact that the sulfuric acid added in the preparation of silica gel, synthesis 26 of Volume II,[1] should be 6 *M* rather than 6 *N* to be consistent with the submitter's statement that "twice the theoretical amount of acid is employed."

Reference

1. R. F. Ruthruff: Inorganic Syntheses, **2,** 95 (1946).

16. ORGANOSILAZANE COMPOUNDS

Submitted by Robert C. Osthoff§ and Simon W. Kantor§

The preparation[1] and properties[2] of a great many organosilicon compounds have been described. However, a relatively small amount of work has been done in the field of silazane chemistry, *i.e.*, the chemistry of compounds which contain at least one silicon-nitrogen bond.[3–8] In general, this group of compounds has been found to be extremely sensitive to hydrolysis. The hydrolytic reaction forms the appropriate amine or ammonia and a silanol and/or a siloxane.

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An interesting structural analogy exists between compounds of the general formula $[(CH_3)_2SiNH]_x$ and the polydimethylsiloxanes, $[(CH_3)_2SiO]_x$. These silazanes differ from the cyclic polydimethylsiloxanes only in that the siloxane oxygen has been replaced by an NH group. However, the chemistry of the silazanes differs from that of the corresponding siloxanes in the ease of hydrolytic cleavage of the Si-N bonds. The silazanes are, in general, volatile, mobile liquids.

It is of interest to observe that the only tertiary amine containing three Si-N bonds that has been isolated to date is trisilylamine, $(H_3Si)_3N$, which was prepared by Stock and Somieski[9] by treating the vapor of chlorosilane with ammonia.

The following syntheses of specific compounds represent general procedures of preparation.

A. HEXAMETHYLDISILAZANE

$$2(CH_3)_3SiCl + 3NH_3 \rightarrow (CH_3)_3SiNHSi(CH_3)_3 + 2NH_4Cl$$

Checked by S. Hashman* and Charles A. Brown*

Hexamethyldisilazane has been prepared by Sauer and Hasek[6,7] from the reaction of ammonia with trimethylchlorosilane in an inert solvent. When the reaction was carried out in liquid ammonia, a somewhat smaller yield of hexamethyldisilazane was obtained, along with appreciable amounts of trimethylsilanol and hexamethyldisiloxane[6] owing to hydrolysis during recovery of the product. Presumably other trimethylhalosilanes could be employed in place of trimethylchlorosilane, but the ready availability of the latter favors its use.

Procedure

The reaction vessel is a 5-l. three-necked round-bottomed flask equipped with ground-glass joints. This flask is fitted with a water-cooled condenser bearing a drying

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tube packed with Drierite (nonindicating Drierite or Dehydrite may be used), a Tru-bore water-jacketed stirrer, and a gas inlet tube extending to about 3 cm. above the level of the liquid in the flask. A large-diameter tube (ca. 13 mm. o.d.) should be employed to prevent plugging with ammonium chloride. The gas inlet tube is connected directly to a tank of liquid ammonia through a suitable trap (to prevent backup) and a mercury blowoff.

Three hundred thirty-five grams of trimethylchlorosilane (3.1 mols) is added to 1500 ml. of anhydrous ethyl ether in the reaction flask, and stirring is commenced. A slow stream of ammonia is allowed to pass into the reaction vessel, and an immediate precipitate of ammonium chloride appears. Slow addition of ammonia is continued for 6 to 8 hours. During the early stages of the ammonia addition, a considerable amount of heat is evolved, and the ether refluxes.

After the addition of the ammonia is completed, the ether is refluxed for 5 hours to remove excess ammonia. The reaction flask is cooled to room temperature, and an additional 1 l. of anhydrous ethyl ether is added. At this time, the ether is removed by filtering, and the ammonium chloride is extracted with four 100-ml. portions of ether. It is desirable but not necessary to carry out these filtrations in a dry box. The combined filtrate is then dried overnight over anhydrous sodium sulfate. The ether is then stripped, and the hexamethyldisilazane is obtained by distillation at atmospheric pressure (b.p. 126°). The yield is 129 to 161 g. (52 to 65%, based upon the trimethylchlorosilane used).

Properties

Hexamethyldisilazane is a colorless mobile liquid boiling at 126°; $n_D^{20} = 1.4080$, $d_4^{20} = 0.7741$.[6] The molar refraction that is observed from these data is 51.44 cc. (calcd. M.R.$_D$ = 51.44 cc.).[10] At 1000 c.p.s., the dielectric constant is 2.27 ± 0.01 at 20°,[10] and the power factor is tan $\delta = 0.0001$.[10]

These values give an Onsager dipole moment of 0.67 D.[10] The Onsager dipole moment of the analogous siloxane, hexamethyldisiloxane, $[(CH_3)_3Si]_2O$, is 0.74 D. at 20°.[11]

Hexamethyldisilazane is rapidly hydrolyzed in contact with the atmosphere.[7] Under carefully controlled conditions, the hydrolysis can be carried out to give substantial yields of trimethylsilanol.[6]

The reaction of hexamethyldisilazane with boron trifluoride forms a white solid which sublimes *in vacuo* at 300 to 315° and reacts rapidly and violently with water.[10] This material approximates $[(CH_3)_3Si]_2NH{\cdot}BF_3$ in composition.[10] The presence of hexamethyldisiloxane formed by exposure of hexamethyldisilazane to atmospheric moisture can be detected readily by examination of the infrared absorption spectra, since the Si-O bond displays a strong absorption at 9.5 μ.[12] This absorption band is not present in the spectrum of pure hexamethyldisilazane.[7]

B. *N*-METHYLHEXAMETHYLDISILAZANE

$$2(CH_3)_3SiCl + 3CH_3NH_2 \rightarrow [(CH_3)_3Si]_2NCH_3 + 2CH_3NH_3Cl$$

Checked by Charles A. Brown*

N-Methylhexamethyldisilazane has been prepared by Sauer and Hasek[7] by the reaction of trimethyl-*N*-methylaminosilane (*N*-1,1,1-tetramethylsilylamine) with trimethylchlorosilane. Larger quantities are more readily prepared by the direct reaction of trimethylchlorosilane with methylamine in an inert solvent.[10]

Procedure

To 2400 ml. of anhydrous benzene in a 5-l. round-bottomed flask equipped with a paddle stirrer, a water condenser, and a gas inlet tube is added 450 g. of trimethylchlorosilane (4.1 mols). The gas inlet tube extends to about 3 cm. above the surface of the reaction mixture

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and is of large size (ca. 13 mm. o.d.) to prevent clogging by amine hydrochloride. Methylamine is allowed to pass through a mercury blowoff and a trap to the gas inlet tube. As soon as a slow stream of amine is started, stirring is commenced. A white precipitate of methylammonium chloride forms at once. The amine is passed into the solution for 8 hours, and then the reaction mixture is refluxed for 18 hours. At the end of this time, the reaction mixture is filtered, and the methylammonium chloride is extracted with two 200-ml. portions of anhydrous benzene. These are filtered and combined with the original benzene solution. After the benzene has been stripped, *N*-methylhexamethyldisilazane is obtained by distillation (b.p. 150° at 1 atm. pressure). The yield is 153 to 175 g. (35 to 40%, based on the trimethylchlorosilane used).

Properties

N-Methylhexamethyldisilazane is a colorless liquid boiling at 150° at 1 atm. pressure; $d_4^{20} = 0.797$, $n_D^{20} = 1.4223$. The dielectric constant at 1000 c.p.s. at 20° is 2.25 ± 0.02, and the power factor is $\tan \delta = 0.001$. From the above data the Onsager dipole moment is calculated to be 0.44 D. The molar refraction is calculated as 56.14 cc., and the observed value using the density and refractive index reported above is 55.92 cc.

C. TRIMETHYL(ANILINO)SILANE

$$(CH_3)_3SiCl + 2C_6H_5NH_2 \rightarrow (CH_3)_3SiNHC_6H_5 + C_6H_5NH_3Cl$$

CHECKED BY LEWIS J. SCHUPP* AND CHARLES A. BROWN*

Trimethyl(anilino)silane has been prepared by the reaction of hexamethyldisilazane with aniline.[13] A more convenient preparation is the direct reaction of trimethylchlorosilane with aniline either in the absence of solvent[14]

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or in the presence of benzene.[10] This reaction is reversible; so it is important to maintain an excess of trimethylchlorosilane.

The replacement of a chlorine by an anilino group has been carried out with chlorosilanes such as dimethyldichlorosilane, methyltrichlorosilane, triethylchlorosilane, and diphenyldichlorosilane. In each case, all of the chlorines are replaced by anilino groups, and yields of 60 to 80% are generally obtained. Whereas an aliphatic amine is readily substituted with 2 mols of trimethylchlorosilane (synthesis 16B), the substitution on aniline stops after one trimethylsilyl group has been introduced. Anilinosilanes are very labile compounds and are especially useful intermediates for the preparation of iodosilanes through the action of hydrogen iodide.[15,16]

Procedure

A solution of 396 g. of trimethylchlorosilane (3.64 mols, 21% excess) in 1500 ml. of anhydrous benzene is placed in a 5-l. round-bottomed flask equipped with a Tru-bore stirrer, a water-cooled condenser, and a dropping funnel, in which is placed a solution of 559 g. of aniline (6.0 mols) in 500 ml. of anhydrous benzene. The stirrer is started, and the aniline solution is added slowly over a period of 1½ hours, during which time a large precipitate of anilinium choride forms. The reaction is maintained at room temperature by the use of an external ice-water cooling bath. At the end of the addition, the mixture is stirred for 2 hours and filtered. The anilinium chloride is washed with 500 ml. of benzene, and the washings are combined with the original benzene solution. After the benzene has been stripped, the residue is distilled under reduced pressure to give recovered aniline, boiling point 93 to 94° at 32 mm. (110 to 210 g., 20 to 38%) and trimethyl(anilino)silane, boiling point 106 to 107° at 24 mm. The yield of product is 230 to 280 g. (46 to 57%). Based on consumed aniline, the yield is 70 to 85%.

Properties

Trimethyl(anilino)silane, boiling point 106 to 107° at 24 mm. and 206° at 760 mm.,[14] is a colorless, mobile liquid; $d_4^{20} = 0.931$ and $n_D^{20} = 1.5219$. The observed molar refraction is 54.15 cc. (calcd. $M.R._D = 54.05$ cc.).[10] The dielectric constant at 1000 c.p.s. is 3.90 ± 0.02 at 20°, and the power factor is $\tan \delta = 0.014$.[10] From these data the Onsager dipole moment is calculated to be 1.37 D.

Trimethyl(anilino)silane is readily hydrolyzed in contact with atmospheric moisture to form aniline. The anilino group is also readily cleaved by anhydrous hydrogen halides, which react instantaneously to form the corresponding trimethylhalosilane and the anilinium halide. Reactions with silicon, germanium(IV), and phosphorus(III) bromides also occur readily to give trimethylbromosilane and the corresponding tetraanilinosilane, tetraanilinogermane, and trianilinophosphine, respectively.[14]

D. HEXAMETHYLCYCLOTRISILAZANE AND OCTAMETHYLCYCLOTETRASILAZANE

$$3(CH_3)_2SiCl_2 + 9NH_3 \rightarrow [(CH_3)_2SiNH]_3 + 6NH_4Cl$$
$$4(CH_3)_2SiCl_2 + 12NH_3 \rightarrow [(CH_3)_2SiNH]_4 + 8NH_4Cl$$

Checked by Vernon Zeitler* and Charles A. Brown*

Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane have been prepared by Brewer and Haber[8] from the reaction of dry, gaseous ammonia with dimethyldichlorosilane in benzene. When the ammonolysis was carried out in liquid ammonia, the combined yield of silazanes was only slightly less, but the trimer was formed in greater proportion than the tetramer. Although the yield of cyclic silazanes was always high, it was difficult to reproduce the proportions of the individual compounds. The procedure given here is an adaptation of that of Brewer and Haber.

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The ammonolysis of other alkyldichlorosilanes has also been realized. Thus, the reaction of diethyldichlorosilane with liquid ammonia produces hexaethylcyclotrisilazane and octaethylcyclotetrasilazane. The reaction of methyldichlorosilane with liquid ammonia also proceeds rapidly to yield high-molecular-weight silazanes from which no simple compounds have been obtained.[8]

Procedure

A solution of 500 g. of dimethyldichlorosilane (3.88 mols) in 3500 ml. of anhydrous benzene is placed in a 5-l. round-bottomed flask equipped with a Tru-bore paddle stirrer, a water-cooled condenser, and a gas inlet tube. The latter extends 12 mm. above the surface of the stirred reaction mixture. The gas inlet tube is connected to a tank of ammonia through a trap (to prevent backup) and a mercury blowoff. An external ice-water bath is used to keep the temperature of the reaction below 30°.

A slow stream of ammonia is allowed to pass into the reaction vessel, and an immediate precipitate of ammonium chloride appears. The addition of ammonia is continued for 8 to 10 hours. In the event that the precipitated ammonium chloride prevents stirring, it is advisable to add an additional 500-ml. portion of anhydrous benzene. After the addition of the ammonia is completed, the reaction mixture is refluxed for 3 hours to remove excess ammonia. The reaction flask is cooled to room temperature, and the copious precipitate of ammonium chloride is removed by filtration. The precipitate is stirred with an additional 500 ml. of anhydrous benzene and filtered. This filtrate is combined with the original benzene filtrate.

The benzene filtrate is stripped to leave 260 to 270 g. (92 to 95%) of crude silazanes. Fractionation of the silazanes gives 103 to 141 g. (36 to 50%) of hexamethylcyclotrisilazane, boiling point 110 to 112° at 85 mm.,[10] and 73 to 120 g. (26 to 42%) of octamethylcyclotetrasilazane, boiling point 134 to 136° at 35 mm.[10] The combined yield of these two cyclic silazanes is usually 210 to 230 g. (74 to 81% of theory based on the dimethyldichlorosilane used).* The octamethylcyclotetrasilazane solidifies in the receiver during distillation. One recrystallization from *n*-hexane (ca. 100 ml. of solvent for 75 g. of silazane) yields purified octamethylcyclotetrasilazane (m.p. 97°). The loss on recrystallization amounts to 10 to 15%.

Properties

Hexamethylcyclotrisilazane, boiling point 111 to 112° at 85 mm. and 188° at 756 mm., is a colorless, mobile liquid which freezes at −10°; $n_D^{20} = 1.4448$, $d_D^{20} = 0.9196$. The observed molar refraction from these data is 63.35 cc. (calcd. $M.R._D = 63.48$ cc.).[10] At 1000 c.p.s., the dielectric constant is 2.57 ± 0.01 at 20°,[10] and the power factor is $\tan \delta = 0.001$.[10] These values give an Onsager dipole moment of 0.92 D.[10] Hexamethylcyclotrisilazane is slowly hydrolyzed in contact with atmospheric moisture with the formation of ammonia and siloxanes.

Octamethylcyclotetrasilazane, boiling point 134.5 to 135.5° at 35 mm. and 225° at 756 mm., is a white solid which melts at 97°. Octamethylcyclotetrasilazane hydrolyzes in moist air to form ammonia and siloxanes.

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* The checkers, on fractionation of the final crude product, found 60 g. of a dark brown liquid which could not be distilled under reduced pressure. It is probable that this is a mixture of higher-molecular-weight silazanes.

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17. ORGANOGERMANIUM COMPOUNDS

By Otto H. Johnson*

Organogermanium compounds are defined, by analogy with organosilicon compounds, as substances having at least one carbon atom attached to a germanium atom. Most of these carbon-containing compounds of germanium may be considered as derivatives of the simple germanes, namely, germane, GeH_4; digermane, Ge_2H_6; and trigermane, Ge_3H_8. Organic derivatives of cyclotetragermane, Ge_4H_8, are known, although cyclotetragermane itself has not yet been isolated.

Nomenclature

Considerable variation is found in the systems of naming organogermanium compounds discussed in the earlier literature. In order that these compounds may be named in compliance with modern standards of uniformity and clarity, the following recommendations are made:

1. Derivatives of germane, digermane, and trigermane are structurally analogous to the first three members of the alkane series and the accepted rules for the nomenclature of such organic compounds[1] should be followed as closely as possible in the naming of comparable germanium compounds.

2. Where organic nomenclature is ambiguous or inapplicable, the germanium compounds should be named in accordance with current recommendations for naming similar silicon compounds.[2,3]

3. Inorganic nomenclature is recommended in accordance with present inorganic usage if such naming is simpler and more specific.

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