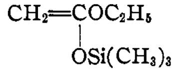
be alkylated with alkyl halides by means of sodium triphenylmethide.[2] We have now found that ethyl isobutyrate and even acetate, which underwent self-condensation instead of being alkylated by benzyl chloride, may be silico-alkylated by the more reactive trimethylchlorosilane.[3] The ester was first converted to its sodio derivative which was then condensed with the chlorosilane (equations 1 and 2).

$$CH_3COOC_2H_5 \xrightarrow[2,\ (CH_3)_3SiCl]{1,\ NaC(C_6H_5)_3} \underset{\mathrm{I}}{(CH_3)_3SiCH_2COOC_2H_5} \quad (1)$$

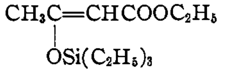
$$(CH_3)_2CHCOOC_2H_5 \xrightarrow[2,\ (CH_3)_3SiCl]{1,\ NaC(C_6H_5)_3} \underset{\mathrm{II}}{(CH_3)_3SiC(CH_3)_2COOC_2H_5} \quad (2)$$

These reactions are assumed to produce the C-derivatives, I and II, rather than the O-derivative, for example, III. The related reaction of sodioacetoacetic ester with triethylchlorosilane has been assumed to form such an O-derivative (IV)[4] but this structure has been questioned.[5]



$$CH_2{=}\underset{OSi(CH_3)_3}{C}OC_2H_5$$

III



$$CH_3C{=}\underset{OSi(C_2H_5)_3}{C}HCOOC_2H_5$$

IV

Evidence that the reaction represented by equation 1 formed structure I is the fact that the product had physical properties practically identical with those reported previously[6] for the silyl ester obtained from the reaction represented by equation 3 which must produce structure I.

$$(CH_3)_3SiCH_2MgCl + ClCOOC_2H_5 \longrightarrow \underset{\mathrm{I}}{(CH_3)_3SiCH_2COOC_2H_5} + MgCl_2 \quad (3)$$

Similar to earlier observations with silyl ester I,[6] silyl ester II was found to undergo cleavage, on refluxing with ethanol, to form ethyl isobutyrate and trimethylethoxysilane. It should be pointed out that the silyl esters obtained in the present work were isolated in the absence of water or acid. When the reaction mixture from sodio ethyl isobutyrate and trimethylchlorosilane was acidified as in the alkylations of esters,[2] only cleavage products, ethyl isobutyrate and hexamethyldisiloxane, were obtained.

Experimental

Trimethylchlorosilane, obtained from the General Electric Co., was used without further purification. Ethyl isobutyrate (Florasynth Laboratories) and ethyl acetate (Eastman Kodak Co.) were dried over Drierite and distilled prior to use.

Sodium triphenylmethide was prepared in ether solution from 3% sodium amalgam and triphenylchloromethane.[7] Triphenylchloromethane, obtained from Columbia Organic Chemicals Co., or prepared in this Laboratory,[8] was recrystallized from benzene; it then melted at 111–113°.

Ethyl Trimethylsilylacetate (I).—A solution of 0.16 mole of sodium triphenylmethide in 750 ml. of ether was transferred under nitrogen pressure[9] to a nitrogen flushed one-liter, three-necked, round-bottomed flask equipped with a sealed stirrer, a dropping funnel, and bulb-type reflux condenser topped with a drying tube. To the stirred dark red solution, cooled to 0° or below by means of an ice–salt-bath, was added rapidly 16.0 g. (0.18 mole) of ethyl acetate in 50 ml. of ether, followed immediately (red color being discharged) by the rapid addition of 20.2 g. (0.184 mole) of trimethylchlorosilane in 50 ml. of ether. After stirring 3 hours and standing 12 hours, the mixture was filtered and the gelatinous precipitate washed thoroughly with ether. The filtrate and washings were concentrated and the precipitate of triphenylmethane removed by filtration and washed with ether. The solvent was removed from the filtrate and washings and the residue distilled through a 15-cm. Vigreux column. The distillate was redistilled through a 21-cm. glass helices-packed column to give 8.2 g. (51%) of recovered ethyl acetate, b.p. 76–78° (n^{20}_{D} 1.3735) and 6.9 g. (27%, 48% based on unrecovered ethyl acetate) of ethyl trimethylsilylacetate, b.p. 74.5° (41 mm.), n^{20}_{D} 1.4150, d^{20}_{4} 0.8761 (reported b.p. 75.5° (42 mm.), n^{20}_{D} 1.4149, d^{20}_{4} 0.8762).[6]

Ethyl Trimethylsilylisobutyrate (II).—This ester was prepared in a manner similar to that described for silyl ester I. To a stirred solution of 0.32 mole of sodium triphenylmethide in 700 ml. of ether at room temperature was added 43.8 g. (0.378 mole) of ethyl isobutyrate in 50 ml. of ether and, after 15 minutes, 40.8 g. (0.376 mole) of trimethylchlorosilane in 50 ml. of ether was added. After stirring one hour and standing 12 hours, the gelatinous precipitate was removed by centrifuging and washed thoroughly with ether. The ether solution was concentrated, the triphenylmethane removed, and the solvent distilled. The residue was distilled through a 30-cm. Vigreux column to give 23.0 g. (52%) of recovered ethyl isobutyrate, b.p. 100–110°, and 22.0 g. (38%, 65% based on unrecovered ethyl isobutyrate) of ethyl trimethylsilylisobutyrate, b.p. 50° (9 mm.), n^{20}_{D} 1.4168, d^{20}_{4} 0.8553; *MR*D calcd.[10] 55.20, found 55.32.

Anal.[11] Calcd. for $C_9H_{20}SiO_2$: C, 57.40; H, 10.70. Found: C, 57.20; H. 10.31.

Treatment of 7.3 g. (0.0388 mole) of silyl ester II with 50 ml. of absolute ethanol, refluxing 4 hours, gave 2.1 g. of material, b.p. 67–70°, which appeared to be an azeotrope of trimethylethoxysilane and ethanol (reported b.p. 66.4°)[12] and 1.2 g. of impure ethyl isobutyrate. None of the original silyl ester was recovered.

Silyl ester II decolorized bromine in carbon tetrachloride within a few minutes. The products were not determined.

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(2) B. E. Hudson and C. R. Hauser, This Journal, **62**, 2457 (1940).

(3) Trimethylchlorosilane is the silicon analog of *t*-butyl chloride but, unlike this alkyl halide which exhibits β-elimination with bases such as ester anions, the chlorosilane undergoes the displacement reaction.

(4) H. Gilman and R. N. Clark, This Journal, **69**, 967 (1947).

(5) F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

(6) J. R. Gold, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 2874 (1948).

(7) W. B. Renfrow and C. R. Hauser, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 607.

(8) C. R. Hauser and B. E. Hudson, *Org. Syn.*, **23**, 102 (1947).

(9) E. Baumgarten and C. R. Hauser, This Journal, **66**, 1039 (1944).

(10) E. L. Warrick, *ibid.*, **68**, 2455 (1946).

(11) Analysis by Clark Microanalytical Laboratory, Urbana, Ill.

(12) R. O. Sauer, This Journal, **66**, 1707 (1944).

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The Reaction of Diphenyldichlorosilane with Ammonia and Amines

By Erik Larsson and Lars Bjellerup

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As part of the investigation of the synthesis and the reactions of aminosilanes[1–7] the reactions of

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(1) E. Larsson and O. Mjörne, *Trans. Chalmers Univ. Technol., Gothenburg*, **87**, 29 (1949).

(2) E. Larsson, *Svensk Kem. Tid.*, **61**, 59 (1949).

(3) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).

(4) E. Larsson, *ibid.*, **4**, 45 (1950).

(5) E. Larsson and B. Smith, *Svensk Kem. Tid.*, **62**, 141 (1950).

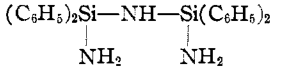
(6) O. Mjörne, *ibid.*, **62**, 120 (1950).

(7) E. Larsson and R. Mårin, *Acta Chem. Scand.*, **5**, 1173 (1951).

diphenyldichlorosilane with ammonia, methylamine, *n*-propylamine, *n*-hexylamine and benzylamine were studied. The following substances were prepared: hexaphenylcyclotrisilazane, diphenyldi-(methylamino)-silane, diphenyldi-(*n*-propylamino)-silane, diphenyldi-(*n*-hexylamino)-silane and diphenyldi-(benzylamino)-silane.

The starting material, diphenyldichlorosilane, was prepared from diphenyldiethoxysilane and benzoyl chloride. Pyridine was used as a catalyst[8] as quinoline was not satisfactory in this case.[9]

The reaction of diphenyldichlorosilane with ammonia was carried out under various conditions: a solution of diphenyldichlorosilane in dry ether was added to liquid ammonia; dry gaseous ammonia was bubbled into a solution of diphenyldichlorosilane in dry ether at 0°, into a boiling solution of diphenyldichlorosilane in dry carbon tetrachloride, and into a boiling solution of diphenyldichlorosilane in dry toluene. From the toluene solution hexaphenylcyclotrisilazane was obtained in good yield. Also from the carbon tetrachloride solution hexaphenylcyclotrisilazane was obtained but in poor yield. The reactions in ether at 0° and at $-33°$ gave no crystalline silicon compounds. However, liquid products were formed which evolved ammonia rapidly on heating and slowly on standing at room temperature. Minute amounts of crystals were deposited on standing at room temperature. The nitrogen content of the primary liquid product was between the values calculated for hexaphenylcyclotrisilazane and for *sym*-tetraphenyldiaminodisilazane



$$\underset{\displaystyle\text{NH}_2}{(\text{C}_6\text{H}_5)_2\text{Si}}-\text{NH}-\underset{\displaystyle\text{NH}_2}{\text{Si}(\text{C}_6\text{H}_5)_2}$$

These observations showed that the reaction of diphenyldichlorosilane with ammonia affords a mixture, the composition of which is determined largely by the reaction conditions. This was in accordance with the results obtained by Larsson and Smith[5] for the reaction between di-*t*-butoxydichlorosilane and ammonia. Analogous observations have been reported by Brewer and Haber[10] and by Schwarz and Weigel.[11]

The hexaphenylcyclotrisilazane was not affected by limited contact with water. It could be dissolved in moist acetone and precipitated with water without decomposition. The nitrogen content of the substance could be determined by dissolving a weighed sample in acetone, adding 0.1 *N* hydrochloric acid, digesting for 18 hours and back-titrating with standard base. Digesting for only a short time gave slightly low values of the nitrogen content. After digesting a weighed sample of hexaphenylcyclotrisilazane for three hours in the manner described, standard base equivalent to the introduced amount of hydrochloric acid was added. From the resulting solution no hexaphenylcyclotrisilazane was recovered. These experiments imply that the action of hydrogen ions on hexaphenylcyclotrisilazane involves an actual cleavage of the Si–N bonds and not only a formation of $-\text{Si}-\overset{+}{\text{N}}\text{H}_2-$ groups (*cf.* Larsson and Mårin[7]).

In accordance with the general exchange reaction

$$\text{R}_3\text{Si}-\text{NH}-\text{R}' + \text{R}''-\text{NH}_2 = \text{R}_3\text{Si}-\text{NH}-\text{R}'' + \text{R}'-\text{NH}_2$$

used by Larsson and co-workers,[2-7] hexaphenylcyclotrisilazane on refluxing with aniline gave diphenyldianilinosilane.

The reactions of diphenyldichlorosilane with methylamine, *n*-propylamine, *n*-hexylamine and benzylamine all gave products of the formula $(\text{C}_6\text{H}_5)_2\text{Si(NHR)}_2$.

Experimental

All experiments were performed with carefully dried solvents and reagents and precautions were taken to exclude moisture from the reaction vessels.

Diphenyldichlorosilane.—A mixture of 27 g. (0.10 mole) of diphenyldiethoxysilane, 84 g. (0.60 mole) of benzoyl chloride and 1 ml. of pyridine was refluxed for eight hours and then subjected to fractional distillation under reduced pressure. After removal of the benzoyl chloride and the ethyl benzoate 19 g. (0.075 mole) of diphenyldichlorosilane was collected at 135° (4 mm.). The chlorine content of the product was determined by dissolving a weighed sample in 96% alcohol and titrating with standard base.

Anal. Calcd. for $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{Si}$: Cl, 28.0. Found: Cl, 27.8.

An experiment performed exactly as above with quinoline instead of pyridine gave a product with a chlorine content of 14.5%. Without a catalyst the reaction gave a product with a chlorine content of only 1.6%.

Hexaphenylcyclotrisilazane.—Into a stirred, refluxing solution of 23 g. (0.091 mole) of diphenyldichlorosilane in 50 ml. of toluene gaseous ammonia was bubbled for five hours. Filtration of the hot mixture and washing with toluene left 10 g. of solid on the filter, which corresponds with the calculated amount of ammonium chloride. From the hot filtrate white crystals precipitated on cooling. They were removed by filtration to give 10 g. (62%) of crystals melting at 211–213°. Recrystallization from 45 ml. of toluene yielded 8.5 g. of hexaphenylcyclotrisilazane melting at 213.5° over a range of 0.3°.

Anal. Calcd. for $\text{C}_{36}\text{H}_{33}\text{N}_3\text{Si}_3$: H, 5.6; N, 7.1; Si, 14.2; mol. wt., 592. Found: H, 5.7; N, 7.0; Si, 14.2; mol. wt. (Rast), 610.

From carbon tetrachloride solution hexaphenylcyclotrisilazane crystallized with one mole of the solvent, which was only partly removed by storage in a vacuum desiccator.

Reaction of Hexaphenylcyclotrisilazane with Aniline.—A mixture of 3.0 g. (0.0051 mole) of hexaphenylcyclotrisilazane and 6.9 g. (0.074 mole) of freshly distilled aniline was refluxed for 18 hours. After cooling 5 ml. of benzene and 5 ml. of (30–50°) petroleum ether were added. During 24 hours in the ice-box crystals formed which were removed, washed with benzene and dried to give 1.3 g. of diphenyldianilinosilane melting sharply at 162°. Anderson reported[12] a melting point of 153° for this compound. We also prepared the substance from diphenyldichlorosilane and aniline in accordance with the directions in Anderson's report and obtained a product which on recrystallization from benzene gave crystals melting at 156–161°.

Diphenyldi-(methylamino)-silane.—To an ice-cooled, vigorously stirred solution of about 1.5 moles of methylamine in benzene a solution of 40 g. (0.16 mole) of diphenyldichlorosilane in 35 ml. of benzene was added dropwise. After all had been added the stirring was continued and the temperature was slowly raised by the removal of the ice-bath. Finally the stirred mixture was heated to refluxing temperature in order to remove all the excess of methylamine. Filtration of the hot mixture and washing with benzene left 22 g. of solid on the filter, which corresponds with the calculated amount of methylamine hydrochloride. From the filtrate benzene was removed by distillation under reduced pressure. The residue was distilled under reduced pressure. A center cut of 27 g. was taken and redistilled as above, giving 8 g. of diphenyldi-(methylamino)-silane

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[8] R. O. Sauer and W. Patnode, THIS JOURNAL, **67**, 1548 (1945).

[9] R. O. Sauer, *ibid.*, **68**, 138 (1946).

[10] S. D. Brewer and C. P. Haber, *ibid.*, **70**, 3888 (1948).

[11] R. Schwarz and F. Weigel, *Z. anorg. allgem. Chem.*, **268**, 291 (1952).

[12] H. H. Anderson, THIS JOURNAL, **73**, 5802 (1951).

collected at 155–156° (3 mm.). Another fraction of 8 g. collected at 157–167° (3 mm.) probably contained a high percentage of diphenyldi-(methylamino)-silane.

Anal. Calcd. for $C_{14}H_{18}N_2Si$: Si, 11.6. Found: Si, 11.5.

Diphenyldi-(*n*-propylamino)-silane.—To a stirred solution of 9.8 g. (0.166 mole) of *n*-propylamine in 50 ml. of toluene a solution of 9.0 g. (0.036 mole) of diphenyldichlorosilane in 15 ml. of toluene was added dropwise. After all had been added the stirring was continued for another 15 minutes and then the mixture was refluxed (with continued stirring) for 15 minutes. After cooling the mixture was filtered and the precipitate washed with toluene to give 6.1 g. of solid on the filter, which corresponds with the calculated amount of *n*-propylamine hydrochloride. After removal of the toluene from the filtrate by distillation under reduced pressure the liquid residue was distilled from a claisen flask giving a center fraction of 7.6 g. (70%) of diphenyldi-(*n*-propylamino)-silane boiling at 178–182° (2 mm.).

Anal. Calcd. for $C_{18}H_{26}N_2Si$: Si, 9.4. Found: Si, 9.6.

The substance could be distilled under atmospheric pressure without decomposition.

Diphenyldi-(*n*-hexylamino)-silane.—This substance was prepared exactly as described for diphenyldi-(*n*-propylamino)-silane from 21 g. (0.21 mole) of *n*-hexylamine and 12 g. (0.047 mole) of diphenyldichlorosilane giving a center fraction of 5.5 g. boiling at 215–230° (3 mm.). On redistillation 1.5 g. of diphenyldi-(*n*-hexylamino)-silane were collected at about 215° (2 mm.).

Anal. Calcd. for $C_{24}H_{38}N_2Si$: Si, 7.3. Found: Si, 7.5.

Diphenyldi-(benzylamino)-silane.—A solution of 13 g. (0.051 mole) of diphenyldichlorosilane in 15 ml. of toluene was run slowly during a period of 15 minutes into a stirred, refluxing solution of freshly distilled benzylamine in 50 ml. of toluene. The mixture was stirred and refluxed for 15 minutes longer. Filtration of the hot mixture and washing with toluene gave 14 g. of solid on the filter, corresponding with the calculated amount of benzylamine hydrochloride. From the filtrate toluene was removed by distillation under reduced pressure at about 30°. The liquid residue was cooled in the ice-box. On scratching with a glass rod crystallization started and proceeded till the whole mass had solidified to yield 20 g. of substance, which was the calculated amount of diphenyldi-(benzylamino)-silane. Recrystallization from 10 ml. of ether yielded 8.4 g. of white crystals, which slowly decomposed on standing in a closed vessel at room temperature. On account of this no defined melting point can be recorded.

Anal. Calcd. for $C_{26}H_{26}N_2Si$: Si, 7.1. Found: Si, 7.4.

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Selenium Dithiocyanate

BY STANLEY M. OHLBERG[1] AND P. A. VANDER MEULEN

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Three investigators[2-4] have reported the reduction of selenious acid to elemental selenium by the reaction between selenious acid and thiocyanic acid. Selenic acid, also, is reduced by the latter reagent to elemental selenium. In a series of experiments designed to study this latter reaction, a yellow crystalline substance was obtained as an intermediate product. The same crystalline product is obtained by the reaction between selenious and thiocyanic acid under certain conditions of temperature, concentration and acidity of the solution.

A survey of the literature revealed that only two investigators have reported compounds containing selenium and a thiocyanogen radical, Baroni[5] has prepared thiocyanogen selenide, $Se_2(SCN)_2$, and thiocyanogen thioselenide, $SeS(SCN)_2$. Ivanov[4] describes thiocyanoselenious acid, $(HSCN)_2 \cdot H_2SeO_3$. An analysis of our crystalline product did not agree with any of the compounds described heretofore, but agreed very closely with the formula for selenium dithiocyanate, $Se(SCN)_2$. The preparation of this new compound, and its properties are described below.

Experimental

1. **Preparation of Selenium Dithiocyanate.**—The best product was obtained by the reaction between selenious acid and thiocyanic acid. A 1.1-g. portion of selenium dioxide[6] was treated with 8.6 ml. of concentrated hydrochloric acid, the mixture was diluted to 50 ml. with water, and cooled to room temperature. Thiocyanic acid was prepared by the method of Gluud, Keller and Klempt[7] and diluted to produce a tenth molar solution. The thiocyanic acid solution was poured, with stirring, into the selenious acid solution, and the mixture was allowed to stand at room temperature for 30 minutes.

The crystals were then collected in a Gooch crucible, excess mother liquor was pressed out by tamping with a glass rod, and the product was washed, first with a little glacial acetic acid, then with anhydrous ether, and tamped again to remove the ether as completely as possible. Finally the product was transferred to a vacuum desiccator containing sodium hydroxide pellets and paraffin shavings. The desiccator was evacuated to 2 mm. and kept in a refrigerator at 5°. The yield was about 70%, based on the SeO_2 used in the preparation.

The compound can also be prepared by bringing together, at room temperature, 50 ml. of a solution containing 1.1 g. of selenium dioxide, 12.9 ml. of concentrated hydrochloric acid, with 50 ml. of another solution containing 3.8 g. of ammonium thiocyanate in water, and allowing the mixture to stand for 30 minutes.

Analysis of the Compound.—Selenium was determined by weighing out a 0.3 to 0.5 g. sample, transferring to a 250-ml. beaker by means of a porcelain spatula (metal is attacked), and dissolving in 10 ml. of concd. nitric acid. The beaker was washed down with distilled water, placed on a steam-bath, and the solution evaporated nearly to dryness. It was then diluted, with 5 *N* hydrochloric acid, hydroxylamine hydrochloride was added, and selenium determined by the procedure described by Hillebrand and Lundell.[8]

Sulfur was determined in the filtrate from the selenium determination. The solution was diluted to 250 ml. and a 50-ml. aliquot was evaporated nearly to dryness on a steam-bath. The subsequent operations were carried out by the method described by Rieman, Neuss and Naiman.[9]

Carbon was determined by a micro method.[10]

For the determination of nitrogen, a 0.5-g. sample was weighed into a Kjeldahl flask, digested with a sulfuric acid–salicylic acid mixture and treated as described by Hillebrand and Lundell.[11]

The results of these determinations are: Calcd. for $Se(SCN)_2$: Se, 40.47; S, 32.86, C, 12.31; N, 14.35. Found: Se, 40.44; S, 32.72; C, 12.5; N, 14.3.

Properties of Selenium Dithiocyanate.—The crystal structure of selenium dithiocyanate has been determined by X-ray diffraction methods. The results will be presented in a separate communication.

Selenium dithiocyanate is fairly stable if kept in a cool, dark place, out of contact with water vapor. The dry compound can be kept for weeks in a tightly stoppered container, in a refrigerator (at 5°). If heated, it decomposes

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(1) From a thesis submitted by Stanley M. Ohlberg to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the Ph.D. degree.

(2) H. A. Ljung, *Ind. Eng. Chem., Anal. Ed.*, **9**, 328 (1937).

(3) W. T. Hall, *ibid.*, **10**, 395 (1938).

(4) V. N. Ivanov, *J. Russ. Phys. Chem. Soc.*, **40**, 661 (1908).

(5) A. Baroni, *Reale Accademia del Lincia*, **23**, 139 (1936).

(6) Best grade, furnished by American Smelting and Refining Co.

(7) W. Gluud, K. Keller and W. Klempt, *Ber.*, **58B**, 1384 (1926).

(8) W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 265.

(9) W. Rieman, J. D. Neuss and B. Naiman, "Quantitative Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 280.

(10) The carbon determinations were performed by Dr. Carl Tiedcke, Teaneck, N. J.

(11) W. F. Hillebrand and G. E. F. Lundell, ref. 8., p. 639.