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Alkoxides of Silicon Containing Silicon–Hydrogen Bonds[1]

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Alkoxysilanes containing more than one hydrogen atom bonded to silicon have been prepared for the first time by two types of reaction. The first is a modified Williamson synthesis and the second a copper-catalyzed reaction between Si–H bonds and alcohols.

In the course of other work with silyl compounds conducted in this Laboratory[2] we have had occasion to prepare substantially molar quantities of monobromosilane and dibromosilane. These reagents are suitable for preparing a variety of compounds containing Si–H bonds, and it was thought that with them we might be able to synthesize monoalkoxysilanes, $H_3Si{-}OR$, dialkoxysilanes, $H_2Si(OR)_2$, and other compounds of this general nature containing more than one Si–H bond. Such compounds have not been reported in the literature. Havill, Joffe and Post[3] succeeded in preparing trialkoxysilanes, $HSi(OR)_3$, from trichlorosilane and alcohols, but they did not report the preparation of compounds representing either of the above types. The reaction of the Si–Br bond either with alcohols or with alkali metal alkoxides should tend to establish Si–OR bonds in their stead. In their preparation of trialkoxysilanes from trichlorosilane and alcohols Havill, Joffe and Post[3] encountered difficulty due to formation at or above room temperatures of tetraalkoxysilanes and hexaalkoxydisiloxanes. They attributed the replacement of the hydrogen of the Si–H bond by an alkoxyl group to the presence of liberated hydrogen chloride which might serve as the agent making the original attack on the Si–H bond with liberation of molecular hydrogen. Even the substitution of a sodium alkoxide for the alcohol did not prevent the displacement of hydrogen; however, the use of benzene as a solvent did aid materially in raising the yields of trialkoxysilanes.

In this Laboratory we encountered difficulties similar to those of Havill, Joffe and Post[3] in our attempts to prepare alkoxy derivatives from the bromosilanes and alcohols. We did, however, succeed in preparing diethoxysilane, dipropoxysilane and dibutoxysilane using a modified Williamson synthesis by treating strictly alcohol-free sodium alkoxides with dibromosilane in accordance with the reaction

$$H_2SiBr_2 + 2NaOR \longrightarrow H_2Si(OR)_2 + 2NaBr$$

It was necessary to use an inert hydrocarbon solvent and a dry nitrogen atmosphere to prevent complete decomposition of the product during the course of the reaction. The yields were low and the products decomposed upon standing in contact with the atmosphere, but these compounds were stable enough to permit distillation under reduced pressure. We were unable to get monobromosilane to react similarly with sodium alkoxides. When alkylbromosilanes (RH_2SiBr) were used instead of monobromosilane it was found possible to replace the bromine atom with an –OR group according to the equation

$$RH_2SiBr + NaOR' \longrightarrow RH_2SiOR' + NaBr$$

Another type of reaction was discovered for establishing Si–OR linkages on silicon atoms already linked to hydrogen. Phenylsilane was found to undergo slight reaction with alcohols upon refluxing a mixture of the reagents for several days. On the other hand, it was found that the addition of copper either in the form of powder taken from a reagent bottle or in the form of rolled copper or brass produced an instant and very vigorous reaction. By adding the alcohol dropwise to a rapidly stirred suspension of copper powder in phenylsilane at room temperature it was possible to control in some measure the extent of substitution of –OR groups for hydrogen atoms in accord with the equations

$$C_6H_5SiH_3 + ROH \xrightarrow{Cu} C_6H_5SiH_2OR + H_2$$

$$C_6H_5SiH_2OR + ROH \xrightarrow{Cu} C_6H_5SiH(OR)_2 + H_2$$

$$C_6H_5SiH(OR)_2 + ROH \xrightarrow{Cu} C_6H_5Si(OR)_3 + H_2$$

It previously has been established[4] that in the presence of alkoxide ions the reaction between alcohols and Si–H bonds goes rapidly to the complete replacement of all Si–H bonds with Si–OR bonds. Copper catalysis thus gives a means for better control of this reaction.

Experimental

Preparation of Monobromosilane and Dibromosilane.—The method of Opitz, Peake and Nebergall[2] was used in preparing these compounds from silane and hydrogen bromide.

Preparation of Alcohol-free Sodium Alkoxides.—The method of Fisher and McElvain[5] was used to assure that the alkoxides prepared were free of any unreacted alcohol. A hot Soxhlet extractor was mounted on one neck of a 2-necked 500-ml. round-bottom flask with the other neck used as an inlet for dry nitrogen. The condenser mounted on the top of the extractor was fitted with an oil trap to serve as a seal and as a flow indicator for gas escaping from the system. The apparatus was flamed out with a Bunsen burner before adding the reagents, and an atmosphere of dry nitrogen was used to protect the alkoxide from decomposition. Approximately 0.2 mole of sodium cut under *o*-xylene was placed in the thimble of the extractor. Approximately 300 ml. of *o*-xylene and 0.2 mole of the appropriate alcohol (previously dried over Drierite) were placed in the extractor flask. The sodium was used in slight excess to

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[1] Taken from a thesis submitted to the Graduate School of Indiana University by Wendell S. Miller in partial fulfillment of the requirements for the degree Master of Arts.

[2] H. E. Opitz, J. S. Peake and W. H. Nebergall, THIS JOURNAL, **78**, 292 (1956).

[3] M. E. Havill, I. Joffe and H. W. Post, *J. Org. Chem.*, **13**, 280 (1948).

[4] J. S. Peake, W. H. Nebergall and Yun Ti Chen, THIS JOURNAL, **74**, 1526 (1952).

[5] N. Fisher and S. M. McElvain, *ibid.*, **56**, 1766 (1934).

assure complete reaction with the alcohol. Upon completion of the reaction the xylene was removed by distillation. The last traces were removed by distillation at 5 mm. pressure. The alkoxide was added to the reaction flask as a slurry in lowboiling petroleum ether.

Preparation of Diethoxysilane.—A 300-ml. 3-necked flask was fitted with a reflux condenser designed for cooling with a Dry Ice–ethanol mixture, a branched inlet tube and a dropping funnel. The branched inlet tube served for the admission of dry nitrogen and of dibromosilane from a brass storage cylinder. About 50 ml. of low-boiling petroleum ether was put into the flask and then 26 g. (0.13 mole) of dibromosilane poured in from the cylinder through the inlet tube after the air in the system had been replaced with dry nitrogen. The sodium ethoxide was shaken with 150 ml. of low-boiling petroleum ether to form a suspension which was added through the dropping funnel a few milliliters at a time over a period of four hours. The reaction mixture was kept at 0° and stirred magnetically by placing the magnetic stirrer under the ice-bath. The reflux condenser prevented the escape of dibromosilane, and the oil seal served as an indicator of any displacement of hydrogen during the course of the reaction.

The petroleum ether solvent was removed by distillation, and the residual liquid was carefully distilled in Metroware equipment under a nitrogen atmosphere. A constant-boiling fraction weighing 3.1 g. (25% yield) distilled at 90–92° (760 mm.). The remaining material boiled below this temperature.

Anal. Calcd. for $C_4H_{12}O_2Si$: C, 40.00; H, 10.00. Found: C, 38.87; H, 9.17.

The product was unstable in air and polymerized to a white solid on standing several days in a sealed sample bottle.

Preparation of Dipropoxysilane.—The same apparatus described above and the same procedure were used for reaction of 0.1 mole of dibromosilane in petroleum ether with 0.2 mole of propanol-free sodium propoxide. Fractionation of the reaction products yielded 5 ml. of material boiling at 136–140° (760 mm.) and 10 ml. of residual material boiling at 190–194° (750 mm.). The material in the lower-boiling fraction apparently underwent some decomposition while awaiting analysis, and the percentages of carbon and hydrogen found did not agree with those calculated for dipropoxysilane. Conditions did not permit the repetition of the experiment. While the existence of dipropoxysilane has not hereby been established, a comparison with the results obtained for the diethoxy and dibutoxy compounds would indicate a high degree of probability for the identity of the 136–140° fraction with dipropoxysilane.

Preparation of Dibutoxysilane.—Sodium butoxide was prepared from 0.24 mole of sodium and 0.18 mole of anhydrous *n*-butyl alcohol using techniques described above. The alkoxide was treated with 0.095 mole of dibromosilane in petroleum ether. The dibutoxysilane distilled at 68–74° (12 mm.). A Rast molecular weight determination in benzene was made in addition to a chemical analysis.

Anal. Calcd. for $C_8H_{20}O_2Si$: C, 54.50; H, 11.43; mol. wt., 176.3. Found: C, 57.21; H, 11.44; mol. wt., 172.5.

The dibutoxysilane was a clear, colorless liquid when first distilled but became cloudy on standing for a few days in a closed bottle.

Preparation of Phenylbromosilane.—A quantity of phenylsilane was prepared by reducing 1640 g. (8 moles) of phenyltrichlorosilane with lithium aluminum hydride according to the reaction

$$4C_6H_5SiCl_3 + 3LiAlH_4 \longrightarrow 4C_6H_5SiH_3 + 3AlCl_3 + 3LiCl$$

The phenylsilane was recovered after hydrolyzing the reaction product and distilling off the solvent from the separated ether solution after it had been dried with Drierite. The phenylsilane (74% yield) distilled at 118–120° (760 mm.). The phenylsilane was brominated by the method of Al-Refai, Peake and Nebergall[6] using hydrogen bromide gas bubbled slowly through an ether solution of phenylsilane. The bromination was conducted on batches of 32.4 g. (0.3 mole) each in 200 ml. of anhydrous ether. The product was purified by distilling off the hydrogen bromide, ether and any unreacted phenylsilane in the presence of 50 ml. of toluene added to the mixture.

Preparation of Cyclohexylbromosilane.—The same techniques were used again whereby cyclohexyltrichlorosilane was first reduced to cyclohexylsilane which was then brominated with hydrogen bromide in ether solution.

Preparation of Phenylmethoxysilane.—Matheson reagent-grade sodium methoxide powder was dried in a vacuum desiccator at 5 mm. pressure for several days prior to use. Its freedom from the presence of alcohol was tested before use by adding a few drops of phenylsilane to the powdered alkoxide. In the presence of alcohol bubbles of hydrogen are liberated due to alkoxide ion catalysis of the reaction[4]

$$C_6H_5SiH_3 + 3HOR \xrightarrow{OR^-} C_6H_5Si(OR)_3 + 3H_2$$

A solution of 0.3 mole of phenylbromosilane in 50 ml. of toluene was placed in a 500-ml. 2-necked flask fitted with a reflux condenser and a dropping funnel. The flask and contents were cooled to 0°. A magnetic stirrer located below the ice-bath provided stirring of the solution during the addition of 10.8 g. (0.2 mole) of sodium methoxide as a slurry in petroleum ether. The slurry was added in small portions from the dropping funnel and had to be repeatedly agitated to keep the stem of the funnel from plugging. The purpose of adding the slurry to the solution rather than *vice versa* was to keep a continual excess of bromosilane in order to reduce to a minimum the chance of reaction of the alkoxide with Si–H bonds. Upon completion of the reaction the mixture was allowed to warm up to room temperature with continuous stirring. The solvents were largely removed by distillation at atmospheric pressure. Phenylmethoxysilane was collected at 60–65° (10 mm.) and phenyldimethoxysilane at 80–85° (10 mm.). A fraction boiling in the range of 125–135° (10 mm.) apparently was a mixture of dimethoxy- and trimethoxyphenylsilane. Redistillation of the lower fractions gave 3 g. (10.5% yield) of the monomethoxy compound and 7 g. (20.6% yield) of the dimethoxy compound.

Anal. Calcd. for $C_7H_{10}OSi$: C, 60.87; H, 7.24. Found: C, 62.25; H, 6.27.

Agreement between calculated and determined percentages of carbon and hydrogen for the dimethoxy compound was less satisfactory than for the monomethoxy compound.

Preparation of Phenylethoxysilane.—Alcohol-free sodium ethoxide was prepared by the method of Fisher and McElvain[5] described above. The method previously described was employed for treating this material with phenylbromosilane. In this case 0.1 mole of phenylbromosilane was mixed with 100 ml. of dry toluene and reacted with a slurry of the ethoxide. Distillation gave a fraction (phenylmonoethoxysilane) boiling at 60–65° (12–14 mm.) and a fraction (phenyldiethoxysilane) boiling at 80–85° (12 mm.). The yield was 3 g. (19.7%) of phenylmonoethoxysilane and 5 g. (25.5%) of phenyldiethoxysilane.

Anal. Calcd. for $C_8H_{12}OSi$: C, 63.15; H, 7.89. Found: C, 65.33; H, 7.50. Calcd. for $C_{10}H_{16}O_2Si$: C, 61.22; H, 8.11. Found: C, 61.84; H, 8.14.

Preparation of Cyclohexylmethoxysilane.—Matheson reagent-grade sodium methoxide was suspended in dry toluene and added gradually by means of a dropping funnel to a toluene solution containing 0.2 mole of cyclohexylbromosilane (prepared as described above). The procedure was the same as described for preparing phenylmethoxysilane. Distillation of the reaction products gave a 4-g. fraction (14% yield) boiling 140–150° (15 mm.) and a high-boiling residue.

Anal. Calcd. for $C_7H_{16}OSi$: C, 59.02; H, 11.11. Found: C, 61.08; H, 9.48.

Reactions between Phenylsilane and Alcohols Catalyzed by Copper.—Into a 500-ml. 2-necked flask fitted with a dropping funnel and a water-cooled reflux condenser were placed in each case the specified amounts of phenylsilane and 2 g. of purified copper powder. The appropriate absolute alcohol was then added dropwise while the mixture was stirred continuously until the alcohol had been added completely. The concentration of alcohol in the mixture was thus kept as low as possible and that of phenylsilane in excess in order to reduce the quantity of phenyltrialkoxysilane formed in the reaction. In each case the mixture was decanted from the copper powder at the end of the reaction and the liquid mixture distilled. Data for the separate experiments are given in Table I.

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(6) I. H. Al-Refai, J. S. Peake and W. H. Nebergall, in preparation.

TABLE I

COPPER-CATALYZED REACTIONS OF PHENYLSILANE WITH ALCOHOLS

Alcohol	Alcohol, moles	Phenylsilane, moles	Products	B.p., °C. Product fractions	Yield, %	$n^{25}D$	d^{25}_4	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
Methyl	0.3	0.3	$C_6H_5SiH_2OCH_3$	60–65 (10 mm.)	26.0	1.4845	1.0051	60.87	59.04	7.24	7.15
			$C_6H_5SiH(OCH_3)_2$	78–84 (10 mm.)	12.0	1.5400	1.0298	57.14	58.24	7.14	7.32
Ethyl	.3	.3	$C_6H_5SiH_2OC_2H_5$	60–67 (10 mm.)	11.1	1.4771	0.9350	63.15	63.55	7.84	7.65
			$C_6H_5SiH(OC_2H_5)_2$	80–84 (10 mm.)	5.0	1.4814	.9533	61.22	62.45	8.11	8.08
n-Propyl	.5	.5	$C_6H_5SiH_2OC_3H_7$	44–48 (5 mm.)	34.1	1.4838	.9430	65.06	64.69	8.43	8.57
			$C_6H_5SiH(OC_3H_7)_2$	90–96 (1.4 mm.)	8.0	1.4781	.9545	65.29	64.50	8.93	8.67
n-Butyl	.5	.5	$C_6H_5SiH_2OC_4H_9$	52–57 (0.7 mm.)	47.4	1.4820	.9408	66.66	65.91	8.88	8.87
			$C_6H_5SiH(OC_4H_9)_2$	90–96 (0.7 mm.)	14.3	1.4785	.9662	66.66	64.90	9.52	8.95

Discussion

This work serves to emphasize the lability of Si–H bonds, particularly in the presence of alkoxyl groups. Their instability in the presence of bases such as OH^- and OR^- is well known. Only by the exercise of extreme care to eliminate moisture and alcohols can an Si–Br bond be replaced with an Si–OR bond in the presence of Si–H. The Si–OR bond is very susceptible to hydrolysis, but this susceptibility appears on the basis of the instability of $H_2Si(OR)_2$ compounds to be enhanced by the existence of Si–H bonds on the same silicon atom. No satisfactory explanation is advanced for the apparent inertness of monobromosilane toward sodium alkoxides.

The action of copper in catalyzing reaction of Si–H bonds with alcohols is not only interesting but makes possible a certain degree of control in the synthesis of silicon alkoxides, so that by proper regulation of the rate of addition of the alcohol one can favor the formation of partially alkoxylated compounds where several hydrogen atoms are attached to the same silicon atom. It was observed that the alkoxylation reactions attempted all took place readily at room temperature but that the vigor of the reaction increased in the order MeOH < EtOH < *n*-PrOH < *n*-BuOH. There was also a detectable tendency to form a higher percentage of the monoalkoxy derivative with the higher alcohols than with those of lower molecular weight.

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[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

The Complexes of Magnesium Ion with Pyrophosphate and Triphosphate Ions

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The stabilities of the complexes of magnesium ion with pyrophosphate ion and triphosphate ion have been calculated from the *p*H lowering due to an excess of magnesium ion during the titration of pyrophosphate ion and triphosphate ion with hydrogen ion. The following complexes and their corresponding over-all complexity constants were obtained at 25° using tetramethylammonium chloride to adjust the ionic strength to unity: $Mg_2P_2O_7$, $\beta_{Mg_2py} = 10^{7.75}$; $MgP_2O_7^{2-}$, $\beta_{Mgpy} = 10^{5.41}$; $Mg(HP_2O_7)^{2-}$, $\beta_{Mg(Hpy)} = 10^{3.06}$; $Mg_2P_3O_{10}^-$, $\beta_{Mg_2tp} = 10^{7.96}$; $MgP_3O_{10}^{3-}$. $\beta_{Mgtp} = 10^{5.83}$; $Mg(HP_3O_{10})^{2-}$, $\beta_{Mg(Htp)} = 10^{3.34}$.

Introduction

This is the fourth paper of a series on the acidity and complexes of polyphosphates.[3–5] A different procedure was used to study the Ca^{2+} complexes due to the lower solubility of the calcium polyphosphates. These results will be reported in a separate paper. That complex formation occurs between calcium and magnesium ions and higher phosphates is well known. However, as indicated by Quimby[6] the evaluation of the complexity constants has been hampered by the limited range of solubility especially in the systems containing calcium ion. Quimby discussed experiments by Gray and Lemmerman[7] in which conductivity measurements were performed according to Job's method of continuous variations. This evidence indicated a 1:1 complex for the complex of calcium ion with triphosphate having a dissociation constant of the order of 3.1×10^{-7} at 30°.

Van Wazer and Campanella[8] have investigated the complexes of magnesium and calcium with higher phosphates with a mean chain length of five phosphate tetrahedra. Their results indicate the dissociation constants for both magnesium and cal-

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(1) Abstracted from the Ph.D. thesis of Sheldon M. Lambert submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1957.

(2) To whom communications should be directed.

(3) J. I. Watters, E. D. Loughran and S. M. Lambert, THIS JOURNAL, **78**, 4855 (1956).

(4) J. I. Watters, S. M. Lambert and E. D. Loughran, *ibid.*, **79**, 3651 (1957).

(5) S. M. Lambert and J. I. Watters, *ibid.*, **79**, 4262 (1957).

(6) O. Quimby, *J. Phys. Chem.*, **58**, 603 (1954).

(7) J. A. Gray and K. E. Lemmerman, unpublished experiments, Research Department, Chemical Division, Proctor and Gamble Co., Miami Valley Laboratory, Cincinnati 31, Ohio.

(8) J. R. Van Wazer and D. A. Campanella, THIS JOURNAL, **72**, 655 (1950).