[Contribution from the Mallinckrodt Chemical Laboratory, Harvard University]

THE PREPARATION OF ORGANOSILANES FROM DICHLOROSILANE

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The first known dialkylsilane, dimethylsilane, was prepared by Stock and Somieski in 1919 (1), by the action of dimethylzinc on dichlorosilane. The lack of availability of dichlorosilane during the intervening years doubtless explains why, of the general class of R_2SiH_2 compounds, only diethyl- (2), di-*n*-propyl- (3), and diphenyl-silane (4) have been reported. The gift of two kilos of dichlorosilane from the Linde Air Products Co. of Tonawanda, N. Y. made possible the preparation of eight disubstituted silanes and a study of their properties. Five of these compounds are new.

These dialkyl- and diaryl-silanes were prepared by passing gaseous dichlorosilane into the appropriate Grignard reagent. The dialkysilanes, and diphenylsilane, are colorless liquids, stable in air. The lower members of the series can be distilled at atmospheric pressure. All of the compounds are unreactive toward pure water; but they are hydrolyzed slowly by acids and rapidly by alkalies, with the liberation of hydrogen and the formation of oily silicone polymers. The dialkylsilanes undergo the usual silane reactions of replacement of the hydrogen by halogens, and by alkyl groups when treated with organolithium compounds. They were unchanged by further treatment with Grignard reagents even under forcing conditions.

The infrared absorption spectra of all of the dialkylsilanes in chloroform solution were measured using a Baird automatic recording infrared spectrophotometer with sodium chloride cell windows. The concentration used was approximately 25 mg. per ml. of chloroform (Figures 1a and 1b). All of the aliphatic disubstituted silanes exhibited a strong sharp absorption peak at 4.77–4.80 microns, while the three aromatic compounds showed the same strong absorption at 4.72–4.77 microns. A band in this region also appears in silane (5) and in dichlorosilane (6), and has been attributed to the Si—H stretching vibration. Silicon compounds other than those containing Si—H bonds, examined for comparison, did not show absorption in this range.

Two other features characteristic of the spectra of all of the disubstituted silanes examined were: first, a single sharp absorption band at 10.6–10.7 microns; and second, one or two strong bands in the region 11.6–12.1 microns. Silane shows an absorption band at 10.86 microns, while dichlorosilane absorbs at 10.5 and 11.35 microns. No other organosilicon compounds examined showed absorption at 10.6–10.7 microns except the alkylsilicon chlorides, which gave broad diffuse absorption throughout this area. Further assignment of these bands must wait for the availability of more related compounds for comparison.

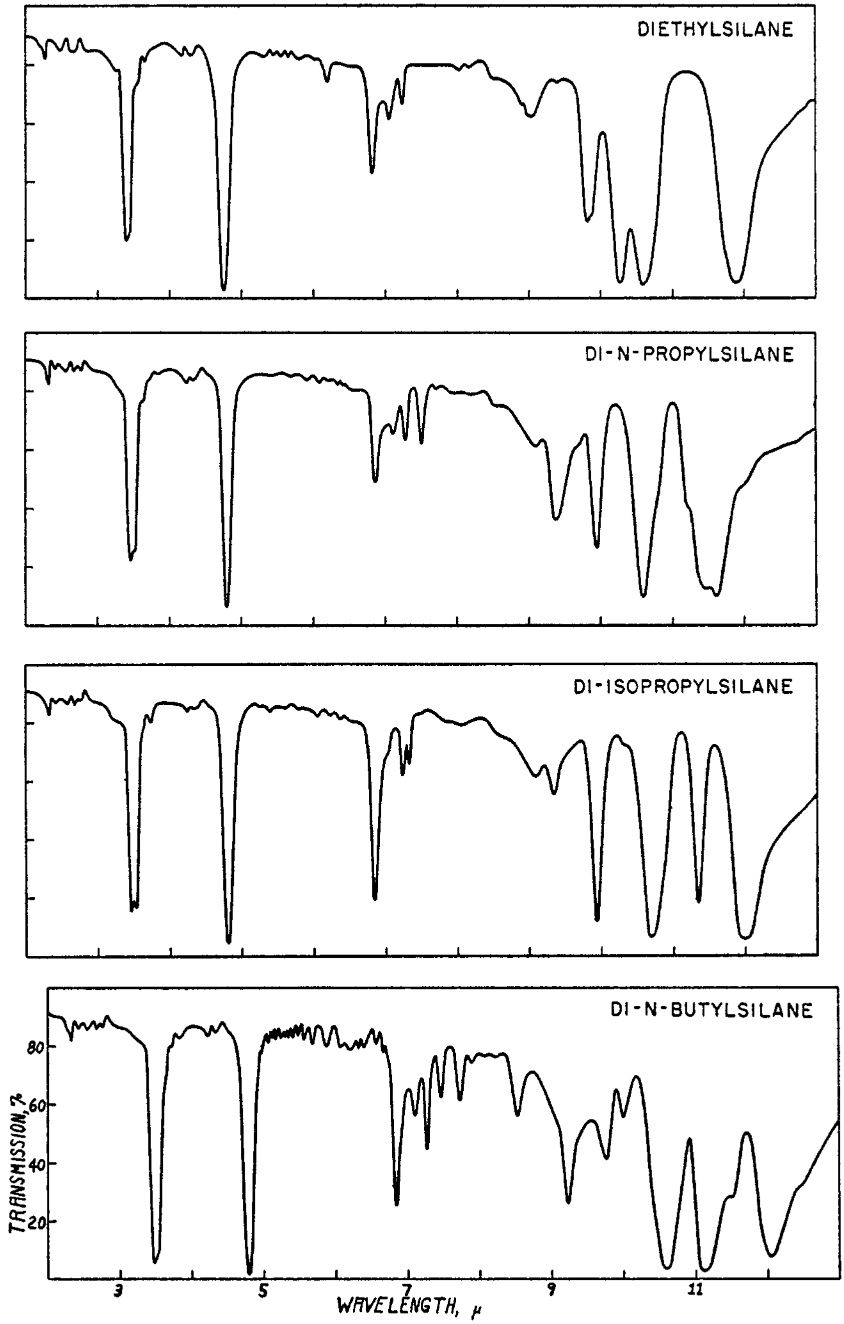

Figure 1a. Infrared Absorption Spectra of Organosilanes

EXPERIMENTAL

All temperatures reported here and in Table I are corrected. Combustion analyses were carried out by Dr. S. M. Nagy and others at the M. I. T. Microanalytical Laboratories.

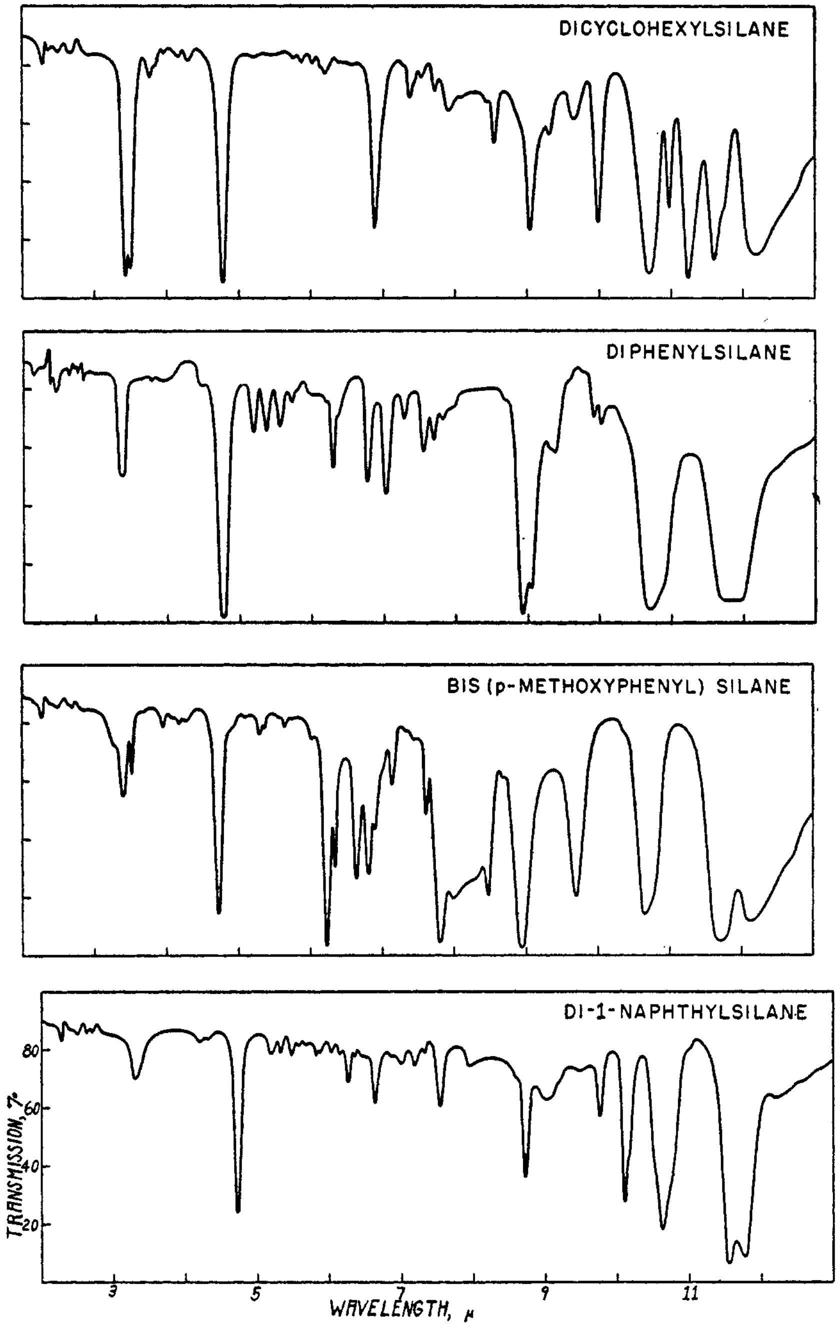

FIGURE 1b. INFRARED ABSORPTION SPECTRA OF ORGANOSILANES

Di-n-butylsilane. A solution n-butylmagnesium bromide was prepared from 68.5 g. (0.50 mole) of Eastman Kodak Co. n-butyl bromide, 14 g. (0.57 mole) of magnesium turnings, and 250 ml. of anhydrous ether. The Grignard solution was refluxed for an hour in an atmosphere of nitrogen, and then decanted into a three-necked flask fitted with a gas inlet tube, a mercury-sealed stirrer, and a reflux condenser. A slight positive pressure of dry nitrogen was maintained on the system through the top of the reflux condenser.

Dichlorosilane was introduced from the previously weighed stainless steel cylinder through the gas inlet tube, which had to be flared at the bottom to prevent plugging by the precipitation of magnesium salts. The gas was added just rapidly enough to cause gentle refluxing of the ether. The cylinder was disconnected and weighed at intervals; addition was ceased after 50 minutes when 25 g. (0.25 mole) of dichlorosilane had been used.

TABLE I

PROPERTIES OF DISUBSTITUTED SILANES, R_2SiH_2

R	B.P., °C.	MM.	n_D^{25}	d_4^{25}	YIELD, %
Ethyl	56	763	1.3917		40
n-Propyl	110.5	769	1.4049		88
Isopropyl	98.5	778	1.4041	0.7085	60
n-Butyl	160	773	1.4221	.7429	49
Cyclohexyl	140–141	23	1.4864	.8890	79
Phenyl	95–97	13	1.580		77
p-Methoxyphenyl	m.p. 57–58.5				47
1-Naphthyl	m.p. 98.5–99				60

TABLE II

ANALYSES OF ORGANOSILICON COMPOUNDS

COMPOUND	FORMULA	ANALYSES			
		C		H	
		Calc'd	Found	Calc'd	Found
Diisopropylsilane	$C_6H_{16}Si$	61.99	62.18	13.88	13.84
Di-*n*-butylsilane	$C_8H_{20}Si$	66.59	66.76	13.97	14.06
Dicyclohexylsilane	$C_{12}H_{24}Si$	73.39	73.82	12.32	12.30
Bis(*p*-methoxyphenyl)silane	$C_{14}H_{16}O_2Si$	68.81	68.59	6.60	6.62
Di-1-naphthylsilane	$C_{20}H_{16}Si$	84.46	84.40	5.67	5.95
Diphenyldi-1-naphthylsilane	$C_{32}H_{24}Si$	88.03	87.74	5.54	5.52

The mixture was then refluxed on a steam-bath for 30 minutes, cooled, and poured slowly into 100 ml. of chilled 10% aqueous acetic acid. The organic layer was separated and extracted with water five times until the washings were neutral to litmus. The ethereal solution was then dried over sodium sulfate and the ether was distilled off from a steam-bath. The oily residue was fractionally distilled through a 50-cm. column packed with stainless-steel helices, at a reflux ratio of 8:1. The yield of colorless product, distilling at 159–161° (773 mm.) was 35 g. (49%).

Diethylsilane, di-n-propylsilane, and *diisopropylsilane* were prepared in the same way. Physical constants and analyses are given in Tables I and II. The lower dialkylsilanes are mobile liquids with somewhat camphorlike odors; they are completely miscible with acetone, ether, chloroform, benzene, and alcohols, but insoluble in water.

Dicyclohexylsilane. This compound was prepared in a manner similar to that for the other dialkylsilanes, but the crude product was distilled from a modified Claisen flask under reduced pressure. The fractions boiling at 136–144° (24 mm.) gave 31 g. (79%) of dicyclohexylsilane. The center cut was redistilled at 23 mm., boiling at 140–141°.

Diphenylsilane. This silane was prepared and purified in the same way as dicyclohexylsilane. The boiling range was 95–97° at 13 mm. Diphenylsilane boils at 257° at 760 mm. pressure; however, attempts to distill this compound, and also dicyclohexylsilane, exposed to air at atmospheric pressure led to flashing and rapid decomposition with the formation of silica.

Both diphenylsilane and dicyclohexylsilane are colorless oily liquids with little odor, miscible with organic solvents but not with water.

Bis(p-methoxyphenyl)silane. A Grignard solution was prepared under nitrogen from 87 g. (0.46 mole) of *p*-bromoanisole and 12 g. (0.5 mole) of magnesium in 300 ml. of anhydrous ether. Using the apparatus previously described, 20 g. of dichlorosilane (0.20 mole) was bubbled in over a period of 85 minutes. The mixture was refluxed for 90 minutes, then cooled and poured onto a mixture of ice and dilute hydrochloric acid. The ether solution was washed with five 100-ml. portions of water and then dried over calcium chloride. The mixture was filtered to remove 0.8 g. of a white solid identified as 4,4′-dimethoxybiphenyl, m.p. 170–174°. The ether was distilled off, and then the residue was heated to 150° for 30 minutes at 25 mm., to remove as much anisole as possible. The residual oil solidified when chilled. Two recrystallizations, one from ethanol and one from methanol, gave 23 g. (48%) of a pale yellowish product melting at 50–54°. Two more recrystallizations from methanol raised the melting point to 57–58.5°. Bis(*p*-methoxyphenyl)silane is highly soluble in all organic solvents tried, except alcohols of low molecular weight.

Di-1-naphthylsilane. This compound was prepared in a manner similar to that for bis(*p*-methoxyphenyl)silane. Distillation of the ether left a yellow oil which solidified on cooling. Two recrystallizations from *n*-propanol gave colorless plates, m.p. 95–97°. The melting point increased to 98.5–99° after two more recrystallizations from ethanol. Di-1-naphthylsilane is readily soluble in benzene, chloroform, acetone, and petroleum ether, sparingly soluble in alcohols, and insoluble in water. Unlike tri-1-naphthylsilane (7), our product was readily hydrolyzed by bases, and a volumetric measurement of the hydrogen evolved on treatment with alcoholic potassium hydroxide gave 98.5% of the volume calculated for complete hydrolysis.

Di-1-naphthyldiphenylsilane. A benzene solution of 9.5 g. (0.033 mole) of di-1-naphthylsilane was added to a slight excess of phenyllithium in ether, prepared according to the directions of Jones and Gilman (8). After refluxing for five hours, the mixture was treated with water to decompose excess phenyllithium and dissolve lithium salts. The ether and benzene were evaporated from the separated organic layer, leaving a resinous residue which was recrystallized three times from ethyl acetate. The yield was 9.7 g. (67%) of white crystals melting at 206.5–207.5°. Gilman and Brannen have previously reported the m.p 194–195° for this compound prepared by a slightly different route (7).

Di-n-propyldibromosilane. To a solution of 6.0 g. (0.052 mole) of di-*n*-propylsilane in 25 ml. of chloroform there was added dropwise 16 g. (0.10 mole) of bromine, also dissolved in 25 ml. of chloroform. The bromine was rapidly decolorized even though the mixture was kept at 0–10° during the addition. The solution was allowed to warm to room temperature and then was refluxed for 30 minutes, while a stream of dry nitrogen was bubbled through to remove hydrogen bromide. The product, a heavy colorless oil, distilled at 204–205° (763 mm.); the yield was 12.0 g. (88%). The compound fumed in moist air and was hydrolyzed rapidly by water and alkalies. The specific gravity at $^{25°}_{4}$ was 1.387. It was analyzed by solution in excess standard sodium hydroxide and back titration with standard acid. No previous preparation of di-*n*-propyldibromosilane was found in the literature.

Anal. Calc'd: Br, 58.3. Found: Br, 58.6, 58.4.

Di-n-butylsilane and ethylmagnesium bromide. Di-*n*-butylsilane (6 g., 0.04 mole) was added to 0.25 mole of ethylmagnesium bromide in 200 ml. of ether. After refluxing for two hours on the steam-bath, the ether was removed almost completely by distillation and replaced with 200 ml. of toluene. The solution was then refluxed at about 100° for 16 hours.

On hydrolysis of the excess ethylmagnesium bromide and distillation of the products 5.6 g. (93.5%) of the di-*n*-butylsilane was recovered unchanged. Other workers have reported unsuccessful attempts to alkylate trisubstituted silanes with Grignard reagents (9).

SUMMARY

By the reaction of Grignard reagents with gaseous dichlorosilane, eight disubstituted silanes have been prepared, in 40–88% yield. The infrared absorption spectra of these compounds have been studied, as well as some of the chemical and physical properties.

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