di-*t*-butylphenoxyaluminohydride ion rather than a steric factor. After this complex with the phenol had been formed, the addition of compound I did not liberate a third equivalent of hydrogen. This showed that I does not exchange with the phenol in the complex ion as such an exchange would lead to the tris-9,10-dihydro-9,10-ethano-9-anthroxyaluminohydride ion as was formed with I acting directly on lithium aluminum hydride.

Methanol liberated hydrogen slowly from the bis-2,6-di-*t*-butylphenoxyaluminohydride ion and, while not quite two equivalents of hydrogen were evolved, no further hydrogen was released upon the addition of hydrochloric acid. This evolution of hydrogen by methanol may be due to exchange or two methoxide ions may be small enough to fit around the aluminum atom together with the 2,6-di-*t*-butylphenoxide ions.

The next stage of hindrance where an excess of a hydroxyl compound would liberate only one equivalent of hydrogen from lithium hydride might be found with an alcohol such as I if substituents were in the 1,8-positions. If bulky enough presumably they could even completely shield the hydroxyl group.

EXPERIMENTAL

Starting materials. The 2,6-di-*t*-butylphenol was a gift of the Ethyl Corporation. The 9,10-dihydro-9,10-ethano-9-anthrol was prepared by condensing anthrone dissolved in pyridine with ethylene at 180° under pressure of about 1500 to 3000 p.s.i. This solvent seems more satisfactory than aqueous sodium hydroxide and dioxane, which were used in our original procedure.[3]

Measurement of hydrogen evolution. A quantitative hydrogenation apparatus was used and solutions were injected with graduated hypodermic syringes. One milliliter of 0.78*M* solution of lithium aluminum hydride in tetrahydrofuran was added to an excess of methanol and 89 ml. of hydrogen was evolved at 25° and 630 mm. When the bridgehead alcohol was used, 66.2 ml. of hydrogen was evolved. A second solution gave 94 ml. of hydrogen with excess methanol and 49 ml. with excess hindered phenol. The values reported are the averages of three runs. No precipitate was observed on mixing either the phenol or the alcohols with the lithium aluminum hydride.

The oxyalumino hydrides. A solution of lithium aluminum hydride in tetrahydrofuran was added to a solution of the alcohol until evolution of hydrogen ceased. Removal of the solvent under reduced pressure gave a white solid whose spectrum in a potassium bromide pellet showed a greatly reduced hydroxyl peak when compared with the starting alcohol. The complex with water gave the starting alcohol back quantitatively with the evolution of hydrogen. Methanol and ethanol also released hydrogen from the complex.

In a similar manner the phenol complex was isolated but on exposure to air quickly turned to a yellow oil. The complex on heating at 80° bubbled and became a yellow oil. The complex liberated hydrogen when treated with water or methanol.

In another experiment 0.80 ml. of a stock solution of lithium aluminum hydride (about 0.75 mmole) was added to a fifty fold excess of methanol and 80.4 ml. of hydrogen was liberated. Next 0.80 ml. of the stock solution was added to 1 g. of 2,6-di-*t*-butylphenol in 8 ml. of tetrahydrofuran and 62.6 ml. of hydrogen was evolved, partly because of drying the solvent and partly from reaction with the phenol. A second addition of 0.80 ml. of the stock solution then liberated 40.6 ml. of hydrogen from the dried solution of excess phenol. After this evolution of hydrogen had ceased, the addition of 1 ml. of methanol liberated an additional 41.4 ml. of hydrogen. This came off slowly over a period of 4 hr. A final addition of hydrochloric acid liberated no further hydrogen.

In a similar experiment the addition of 2 g. of the alcohol I to the phenol complex did not liberate any hydrogen while subsequent addition of methanol did.

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[3] J. S. Meek, V. C. Godefroi, and W. B. Evans, abstracts, 123rd meeting of the American Chemical Society 27M, 1953. See also M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta,* 40, 2129 (1957).

Some Alkoxyorganosilanes[1]

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In the course of an investigation of organosilicon polymers containing bulky organic groups, we have prepared several organoalkoxysilanes whose synthesis and properties have not been reported elsewhere. Each of the compounds was obtained from the well known condensation of an aryl Grignard reagent with either an alkoxysilane or an alkoxychlorosilane.

Two of the new compounds, 4-chlorophenylethoxydiphenylsilane and 4-chlorophenylethoxydimethylsilane, were prepared for an investigation of the synthesis of monomers of the type $(C_2H_5OSiR_2C_6H_4)_4Si$, where R is methyl or phenyl. Treating either compound with silicon tetrachloride in the presence of sodium in diethyl ether failed to initiate a reaction. When boiling toluene was used as the solvent, considerable cleavage of the ethoxyl groups occurred and pure products could not be isolated from the reaction mixture.

The other new compounds—diethoxymethyl-1-naphthylsilane, diisopropoxymethyl-1-naphthylsilane, diethoxymethyl-2-naphthylsilane, and 2-biphenylyldiethoxymethylsilane—were prepared for an investigation of the effect of bulky pendant aromatic groups on the formation of siloxane chains. Also used in this investigation was 4-biphenylyldiethoxymethylsilane whose preparation has been described elsewhere.[2] An attempt to prepare 9-

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

[2] L. W. Breed, *J. Org. Chem.,* 25, 1198 (1960).

anthryldiethoxymethylsilane was not successful. Although the Grignard reagent of 9-bromoanthracene in tetrahydrofuran was obtained in good yield, a condensation with chlorodiethoxymethylsilane could not be effected.

Initial attempts to prepare the second group of monomers utilized dialkoxychloromethylsilanes in the condensation with the aryl Grignard reagents. 2-Naphthylmagnesium bromide and 2-biphenylylmagnesium bromide failed to condense preferentially with the silicon-attached chlorine in chlorodiethoxymethylsilane. Considerable hydrolyzable chlorine remained, particularly in the naphthyl derivative, but methyltriethoxysilane, condensed with 2-naphthylmagnesium bromide, gave a pure product with no loss of yield.

For polymer preparation a two-step procedure was followed. First the monomers were hydrolyzed in a mixture of ethanol and benzene in the presence of hydrochloric acid. The hydrolysis products were then treated with a catalytic amount of sodium hydroxide at 145° for five hours following a method similar to that described by Hyde[3] and Andrianov[4] for preparing linear siloxanes. During the second procedure cleavage products, naphthalene and biphenyl, were obtained as sublimates in the reaction flask.

The molecular weights of the polymers from diethoxymethyl-2-naphthylsilane and 4-biphenylyldiethoxymethylsilane did not differ greatly from the molecular weight of a polymer prepared from diethoxymethylphenylsilane under similar conditions (see Table I). All values were in the neighborhood of 2000, outside the limit of precise determination by the cryoscopic methods. In the case of the materials prepared from 2-biphenylyldiethoxymethylsilane and diethoxymethyl-1-naphthylsilane, however, molecular weights were less, the bulky pendant groups interfering with the growth of the siloxane chain. This effect is not surprising in view of the reported steric effects in the hydrolysis and condensation of silane monomers with bulky substituents such as *t*-butyl and trimethylsilylmethyl.[5-7]

All the biphenylyl- and naphthylsiloxanes were solids at room temperature. The product obtained from 4-biphenylyldiethoxymethylsilane melted rather sharply near 100°. The others became somewhat tacky below their melting points, and softened over a greater range. Only the latter polymer was a solid before the alkali treatment, the others were tacky semisolids.

TABLE I

MOLECULAR WEIGHTS AND SOFTENING POINTS OF POLYMERIC SILOXANES

Polymer from:	Molecular Weight	Softening Point
Methylphenyldiethoxysilane	2020 1890	Liquid
2-Biphenylylmethyldiethoxysilane	880 910	55
4-Biphenylmethyldiethoxysilane	2130 2620	100
Methyl-1-naphthyldiethoxysilane	1190 1260	65
Methyl-2-naphthyldiethoxysilane	1800 1840	55

EXPERIMENTAL

4-Chlorophenylethoxydiphenylsilane. In a 3-l. flask were placed 26.4 g. (1.1 g.-atoms) of magnesium turnings, 20 g. of *p*-bromochlorobenzene, and 100 ml. of diethyl ether. To the mixture a solution containing 171.4 g. (total 1 mole) of *p*-bromochlorobenzene, 272.4 g. (1 mole) of diethoxydiphenylsilane, and 400 ml. of diethyl ether was added dropwise over a 3.5-hr. period. The product was refluxed 22 hr., cooled, filtered and stripped to remove the solvents. Fractional distillation of the residue at 0.25 mm. gave 38.5 g. of diethoxydiphenylsilane boiling at 104–108° and 169 g. (49.9%) 4-chlorophenyldiphenylethoxysilane boiling at 158–160°, d_4^{25} 1.038; n_D^{25} 1.4938.

Anal. Calcd. for $C_{10}H_{15}ClOSi$: C, 56.40; H, 7.04; Cl, 16.50; Si, 13.10; MR_D, 60.33. Found: C, 56.20; H, 6.93; Cl, 16.47; Si, 13.12; MR_D, 60.22.

4-Chlorophenylethoxydimethylsilane. In a similar procedure, 26.4 g. (1.1 g.-atoms) of magnesium turnings, 191.4 g. (1.0 mole) of *p*-bromochlorobenzene, and 148.2 g. (1.0 mole) of diethoxydimethylsilane in 500 ml. ether gave 123 g. (57.3%) of 4-chlorophenyldimethylethoxysilane boiling at 65–68° at 0.25 mm., d_4^{25} 1.132; n_D^{25} 1.5887.

Anal. Calcd. for $C_{20}H_{19}ClOSi$: C, 71.20; H, 5.65; Cl, 11.47; Si, 8.26; MR_D, 99.97. Found: C, 71.09; H, 5.52; Cl, 11.47; Si, 8.26; MR_D, 100.00.

9-Anthrylmagnesium bromide. In a 250-ml. flask were placed 0.5 g. (0.021 g.-atom) of magnesium turnings, 2.57 g. (0.01 mole) of 9-bromoanthracene, 20 ml. of tetrahydrofuran, and a small crystal of iodine. The mixture was heated 2 hr., cooled, and filtered through glass wool into 15% hydrochloric acid. The product, recrystallized from benzene, gave 1.2 g. (67%) anthracene melting 212–215°.

9-Anthryldiethoxymethylsilane (attempted). A 250-ml. flask was charged with 1.46 g. (0.06 g.-atom) of magnesium turnings, 1.0 g. of 9-bromoanthracene, 10 ml. of tetrahydrofuran, and a crystal of iodine. A mixture containing 6.71 g. (0.03 mole, total) of 9-bromoanthracene, 5.05 g. (0.03 mole) of methylchlorodiethoxysilane, and 25 ml. of tetrahydrofuran was added dropwise over a period of 45 min. Heating, which was required throughout the addition, was continued for 4.5 hr. At the end of the heating period 40 ml. of methylcyclohexane was added, and a part of the tetrahydrofuran was removed by distillation. A dark-colored oil remained which was insoluble in benzene and solidified on cooling. No 9-anthryldiethoxymethylsilane was obtained in attempts to purify the crude product.

In similar trials no product was obtained when the reaction mixture was refluxed 16 hr. or when the tetrahydrofuran was replaced with di-*n*-butyl ether and the mixture refluxed for 14 hr. at 142°.

Diethoxymethyl-1-naphthylsilane. 1-Naphthylmagnesium bromide, prepared from 32.5 g. (0.157 mole) of 1-bromonaphthalene and 5.8 g. (0.239 g.-atom) of magnesium

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[3] J. F. Hyde, U. S. Patent 2,542,334 (1951).

[4] K. A. Andrianov, *Organic Silicon Compounds*, Moscow, 1955. (United States Department of Commerce, Office of Technical Services Translation), p. 763.

[5] L. H. Sommer and L. J. Tyler, *J. Am. Chem. Soc.*, **76**, 1030 (1954).

[6] L. H. Sommer, R. M. Murch, and F. A. Mitch, *J. Am. Chem. Soc.*, **76**, 1619 (1954).

[7] D. Seyferth and E. G. Rochow, *J. Polymer Sci.*, **18**, 543 (1955).

turnings in 43.2 g. (0.6 mole) of tetrahydrofuran and diluted with 85 ml. of tetrahydrofuran, was cooled to 6° with an ice bath and treated with 30.3 g. (0.18 mole) of methylchlorodiethoxysilane. The temperature of the mixture was not allowed to exceed 10° during the addition. After the addition was complete, the product was refluxed 1 hr., diluted with heptane, concentrated by distillation, and filtered. Fractional distillation gave 23.6 g. (58%) of diethoxymethyl-1-naphthylsilane boiling at 114–115° at 0.1 mm., n_D^{25} 1.5393; d_4^{26} 1.039.

Anal. Calcd. for $C_{15}H_{20}O_2Si$: Si, 10.79; MR_D, 78.46. Found: Si, 10.44; MR_D, 78.42.

In a repetition of the experiment with 0.7 mole of 1-bromonaphthalene, the bromide and the silane were added to the reaction mixture concomitantly. The yield of methyl-1-naphthyldiethoxysilane boiling at 100° at 0.05 mm. was 36%.

Diisopropoxymethyl-1-naphthylsilane. When 5.9 g. (0.24 g.-atom) of magnesium was treated with a mixture of 41.4 g. (0.2 mole) of 1-bromonaphthalene, 47.2 g. (0.24 mole) of methylchlorodiisopropoxysilane, and 43.2 g. (0.6 mole) of tetrahydrofuran, diisopropoxymethyl-1-naphthylsilane (37.5%) was obtained boiling 137–143° at 2.7 mm., n_D^{25} 1.5165, d_4^{25} 0.996.

Anal. Calcd. for $C_{17}H_{24}O_2Si$: Si, 9.74; MR_D, 87.72. Found: Si, 9.99; MR_D, 87.46.

Diethoxymethyl-2-naphthylsilane. A mixture of 20.0 g. of 2-bromonaphthalene, 24.9 g. (0.145 mole) of chlorodiethoxymethylsilane, and 20 ml. of ethyl ether was added dropwise to a flask containing 5.0 g. (0.121 mole, total) of 2-bromonaphthalene, 5 ml. of ether, and 5.0 g. (0.206 g.-atom) of magnesium turnings. The contents of the flask were heated under reflux and stirred for 19 hr., and then cooled and filtered. Distillation at 0.5 mm. gave 15.1 g. of unchanged 2-bromonaphthalene between 70° and 99°. Fractional distillation of the remainder of the material gave about 4 g. (13%) of impure diethoxymethyl-2-naphthylsilane boiling 138–138.5° at 2.5 mm., n_D^{25} 1.5518, d_2^{25} 1.066.

Anal. Calcd. for $C_{15}H_{20}O_2Si$: Si, 10.79; MR_D, 78.46. Found: Si, 11.37; MR_D, 78.01.

The product fumed in air and gave a positive Beilstein test. Titration of a hydrolyzed aliquot indicated that the product contained 5.32 weight per cent chlorine, or that about one-third of the material was chloroethoxymethyl-2-naphthylsilane.

A product of about the same purity and in about the same yield was obtained when the reaction was carried out in tetrahydrofuran.

Repetition of the procedure with 25.0 g. of methyltriethoxysilane in place of the methylchlorodiethoxysilane gave 4.6 g. (15%) of diethoxymethyl-2-naphthylsilane boiling 140–144° at 2.2 mm., n_D^{26} 1.5407, d_4^{26} 1.042. About 17 g. of 2-bromonaphthalene was recovered unchanged.

Anal. Found: Si, 10.93; MR_D, 78.53.

2-Biphenylylmethyldiethoxysilane. When 9.6 g. (0.40 g.-atom) of magnesium was treated with a mixture of 76.7 g. (0.33 mole) of 2-bromobiphenyl, 67.5 g. (0.40 mole) of chlorodiethoxymethylsilane, and 71.3 g. (0.99 mole) of tetrahydrofuran and the product was worked up similarly, 42.1 g. (45%) 2-biphenyldiethoxymethylsilane boiling 102° at 0.04 mm. was obtained, n_D^{25} 1.5334, d_4^{25} 1.094.

Anal. Calcd. for $C_{15}H_{22}O_2Si$: Si, 9.81; MR_D, 85.27. Found: Si, 9.84; MR_D, 84.64.

Titration of a hydrolyzed aliquot indicated that the product contained 0.36 weight per cent hydrolyzable chlorine.

Hydrolysis procedure. A mixture of 5 ml. of 95% ethyl alcohol, 5 ml. of concd. hydrochloric acid, and 10 ml. of the silane monomer was refluxed 2 hr., diluted with 15 ml. of benzene, and refluxed for an additional 4 hr. The product, washed with water until it was neutral, was heated to 100° *in vacuo* to remove the solvents.

Rearrangement of the siloxanes with sodium hydroxide. Five grams of the polymer and 0.2 g. of 50% sodium hydroxide was heated at 145° for 5 hr. The cooled product, diluted with 20 ml. of benzene, was washed with portions of water until the washings were neutral, and then heated at 100° overnight *in vacuo.* In each case a cleavage product, either naphthalene or biphenyl, was collected as a sublimate during the initial heating period. Although no attempt was made to recover the decomposition products quantitatively, the solid material recovered usually represented about 5% of the organic groups present in the polymer.

Polymer molecular weights given in Table I were determined cryoscopically in benzene, $K_f = 5.32$. Softening points of the four polymers were determined as follows: A few milligrams of the sample was placed between two-micro cover glasses on a Fisher-Johns melting point apparatus heated at the rate of 5°/min. A slight pressure was applied on the top cover glass, and the temperature at which the material flowed freely between the plates was recorded. These results are also recorded in Table I.

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Reactions of Triphenylsilyllithium with Triaryl Phosphates

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Recent publications[1,2] from this laboratory described the reactions of triphenylsilyllithium with trialkyl phosphates. High yields of alkyltriphenylsilanes were realized when the reactions were carried out in a 1:1 mole ratio. The use of three equivalents of triphenylsilyllithium in attempts to utilize all three alkyl groups of tri-*n*-butyl phosphate in this reaction, however, resulted in the isolation of considerable amounts of hexaphenylisildane together with other products.[2] A mechanism involving the displacement of a butoxyl group, and the subsequent cleavage of the intermediate silylphosphorus compound by triphenylsilyllithium, was proposed to account for the formation of the disilane.

The reactions of triphenylsilyllithium in various ratios with triaryl phosphates, likewise gave sizeable amounts of hexaphenyldisilane. After hydrolysis, the reaction mixtures had pronounced phosphine-like odors, as did the 3:1 reactions of triphenylsilyllithium with tri-*n*-butyl phosphate.[2] Thus, it appears as though a similar mechanism is involved in these reactions.

This reaction path is not surprising since carbon-metallic compounds react with substances having the P—O—R linkage *via* displacements of —O—R groups from phosphorus.[3] Furthermore, resonance

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[1] M. V. George, B. J. Gaj, and H. Gilman, *J. Org. Chem.*, 24, 624 (1959).

[2] H. Gilman and B. J. Gaj, *J. Org. Chem.* (in press).

[3] For references to reactions of this type, see the publication cited in ref. (2) of this paper.