Dinitrate Ester: n^{20}_{D} 1.4688, d^{20}_{20} 1.191. *Anal.* Calcd. for $C_{11}H_{18}N_2O_8$: C, 43.14; H, 5.92; N, 9.15. Found: C, 42.95; H, 6.08; N, 8.82.

Monoallyl Pentaerythritol Ether: b.p. 148–150° (1 mm.), n^{20}_{D} 1.4843, d^{20}_{20} 1.135, was obtained in 35% yield. *Anal.* Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.50; H, 9.12.

Trinitrate Ester: n^{20}_{D} 1.4797, d^{20}_{20} 1.373. *Anal.* Calcd. for $C_8H_{13}N_3O_{10}$: C, 30.87; H, 4.21; N, 13.50. Found: C, 31.01; H, 3.93; N, 13.53.

Monopropyl Pentaerythritol Ether.—A solution of 35.2 g. of monoallyl pentaerythritol ether in 400 ml. of 95% ethanol was hydrogenated at room temperature and atmospheric pressure, using 0.2 g. of platinum oxide. The product was distilled at 125° (1 mm.), n^{20}_{D} 1.4662, d^{20}_{20} 1.096. *Anal.* Calcd. for $C_8H_{18}O_4$: C, 53.91; H, 10.18. Found: C, 53.57; H, 10.25.

Trinitrate Ester: n^{20}_{D} 1.4654, d^{20}_{20} 1.332. *Anal.* Calcd. for $C_8H_{15}N_3O_{10}$: C, 30.67; H, 4.83; N, 13.42. Found: C, 30.67; H, 4.77; N, 13.65.

Dipropyl Pentaerythritol Ether.—A solution of 25 g. of diallyl pentaerythritol in 175 ml. of 95% ethanol was hydrogenated at room temperature and atmospheric pressure, using 0.2 g. of platinum oxide. The product was distilled at 115° (1 mm.), n^{20}_{D} 1.4461, d^{20}_{20} 0.993. *Anal.* Calcd. for $C_{11}H_{24}O_4$: C, 59.97; H, 10.98. Found: C, 59.83; H, 11.06.

Dinitrate Ester: n^{20}_{D} 1.4470, d^{20}_{20} 1.144. *Anal.* Calcd. for $C_{11}H_{22}N_2O_8$: C, 42.57; H, 7.15; N, 9.03. Found: C, 42.59; H, 7.15; N, 9.15.

Monoglycerol Pentaerythritol Ether.—A mixture of 15 g. of monoallyl pentaerythritol ether, 100 ml. of 95% ethanol and 0.015 g. of osmium tetroxide dissolved in 5 ml. of water was placed in a three-necked flask equipped with a stirrer and dropping funnel. The temperature of the mixture was adjusted to 20° and 100 g. of cold 3% hydrogen peroxide was added dropwise with slow stirring. The reaction mixture was maintained at 0° overnight, then concentrated and subjected to molecular distillation. The distillate formed sugar-like crystals which softened at 55° and melted at 59–61°. *Anal.* Calcd. for $C_8H_{18}O_6$: C, 45.71; H, 8.64. Found: C, 45.91; H, 8.63.

Pentanitrate Ester: m.p. 54.5–55.0°; n^{31}_{D} 1.531, 1.520; d^{20}_{20} 1.57. *Anal.* Calcd. for $C_8H_{13}N_5O_{16}$: C, 22.03; H, 3.00; N, 16.09. Found: C, 22.15; H, 2.97; N, 15.92.

Diglycerol Pentaerythritol Ether.—Diglycerol pentaerythritol ether was prepared by hydroxylating diallyl pentaerythritol ether. The method of preparation was similar to that used for the preparation of monoglycerol pentaerythritol ether from monoallyl pentaerythritol ether. The product crystallized after molecular distillation, m.p. 72.5–74.0°, softening at 69°, when heated rapidly (Fisher-Johns melting point apparatus). *Anal.* Calcd. for $C_{11}H_{24}O_8$: C, 46.47; H, 8.51. Found: C, 46.67; H, 8.43.

Hexanitrate Ester: n^{20}_{D} 1.4878, d^{20}_{20} 1.540. *Anal.* Calcd. for $C_{11}H_{18}N_6O_{20}$: C, 23.83; H, 3.27; N, 15.16. Found: C, 23.96; H, 3.08; N, 14.87.

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Functional Aromatic Silanes

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RECEIVED SEPTEMBER 4, 1952

The preparation of aromatic silane derivatives containing nuclear substituted functional groups has been the subject of a series of recent investigations.[1–6]

Roberts, McElhill and Armstrong[1] described the preparation of *m*- and *p*-trimethylsilylbenzoic acid (I) *via* the Grignard reaction as well as by means of the corresponding lithium derivative.

In the present investigation the preparation of the *p*-trimethylsilylbenzoyl chloride (II) and the corresponding amide (III) was undertaken. The synthesis of the *p*-trimethylsilylbenzoyl chloride presented somewhat of a problem because of the well-known tendency of silyl groups connected to an aromatic ring to undergo cleavage in acid medium particularly at elevated temperatures. It therefore became necessary to adopt a procedure using mild conditions and working if possible at low temperatures. This was accomplished by using thionyl chloride in the presence of pyridine as a hydrohalogen acceptor

$$\underset{\text{I}}{(CH_3)_3SiC_6H_4COOH} + SOCl_2 \xrightarrow{\text{pyridine}} \underset{\text{II}}{(CH_3)_3SiC_6H_4COCl}$$

The above reaction required less than ten minutes and the resulting acid chloride reacted with an excess of cold concd. ammonium hydroxide which yielded instantly the corresponding amide (III).

$$\underset{\text{II}}{(CH_3)_3SiC_6H_4COCl} + NH_4OH \longrightarrow \underset{\text{III}}{(CH_3)_3SiC_6H_4CONH_2}$$

Silicon-containing aromatic aldehydes have hitherto not been reported in literature. *p*-Trimethylsilylbenzaldehyde (VI) was prepared by reaction of *p*-trimethylsilylphenylmagnesium bromide (IV) with ethyl orthoformate followed by hydrolysis of the resulting acetal (V)

$$\underset{\text{IV}}{(CH_3)_3SiC_6H_4MgBr} + HC(OC_2H_5)_3 \longrightarrow \underset{\text{V}}{(CH_3)_3SiC_6H_4CH(OC_2H_5)_2} \longrightarrow \underset{\text{VI}}{(CH_3)_3SiC_6H_4CHO}$$

The acetal was not isolated in pure form but was used directly in the hydrolysis step to yield the aldehyde (VI). Remarkable is the fact that *p*-trimethylsilylbenzaldehyde can be steam distilled from an acid solution without undergoing cleavage of the C (phenyl)–Si bond.

The synthesis of silicon-containing phenols is of very recent origin. Gilman and Nobis[7] in 1950 reported several unsuccessful attempts to prepare *o*- and *m*-trimethylsilylphenol by various methods and concluded that such phenols were unstable structures.

Sunthankar and Gilman,[8] however, succeeded in preparing trimethyl- and triphenylsilylnaphthols by the reaction of chlorosilanes with the corresponding naphthyllithium compounds.

After the present work was completed Speier[2] reported the successful synthesis of *o*- and *p*-trimethylsilylphenol by the reaction of *o*- and *p*-chlorophenoxytrimethylsilane with sodium and trimethylchlorosilane. The same investigator also reported that magnesium could not be used in place of sodium when used with *p*-bromophenoxytrimethylsilane.

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(1) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2925 (1949).

(2) J. L. Speier, *ibid.*, **74**, 1003 (1952).

(3) R. A. Benkeser and P. E. Brumfield, *ibid.*, **73**, 4770 (1951).

(4) D. W. Lewis and G. C. Gainer, *ibid.*, **74**, 2931 (1952).

(5) B. N. Dolgov and O. K. Panina, *Zhur. Obshchei Khim.* (*J. Gen. Chem.*), **18**, 1129 (1948); *C. A.*, **43**, 1737 (1949).

(6) A. J. Barry and J. W. Gilkey, U. S. Patent 2,601,237 (1952).

(7) H. Gilman and J. F. Nobis, THIS JOURNAL, **72**, 2629 (1950).

(8) S. V. Sunthankar and H. Gilman, *ibid.*, **72**, 4884 (1950).

In the present work the Grignard reagent of *p*-bromophenoxytrimethylsilane (VII) reacted with trimethylchlorosilane

$$\underset{\text{VII}}{(CH_3)_3SiOC_6H_4MgBr} + (CH_3)_3SiCl \longrightarrow \underset{\text{VIII}}{(CH_3)_3SiOC_6H_4Si(CH_3)_3}$$

The hydrolysis of (VIII) to the free phenol (IX) was accomplished by treatment with acidified dilute ethanol

$$\underset{\text{VIII}}{(CH_3)_3SiOC_6H_4Si(CH_3)_3} \longrightarrow \underset{\text{IX}}{HOC_6H_4Si(CH_3)_3}$$

Experimental

***p*-Trimethylsilylbenzoic acid** (I) was prepared *via* the Grignard reaction using essentially the procedure of Roberts, McElhill and Armstrong.[1] The pure compound crystallized in colorless needles, m.p. 117–118° (uncor.).

***p*-Trimethylsilylbenzoyl Chloride** (II).—In an erlenmeyer flask was placed 11.5 g. of *p*-trimethylsilylbenzoic acid, 4.7 g. of pyridine and 75 cc. of ether. A solution of 7.1 g. of thionyl chloride in 100 cc. of ether was gradually added with shaking. A white precipitate formed. After shaking for about ten minutes, pyridine hydrochloride was filtered off and the ethereal solution of the acid chloride was used directly for the preparation of the amide.

***p*-Trimethylsilylbenzamide** (III).—The ethereal solution of the acid chloride (II) was added dropwise to an excess of concd. ammonium hydroxide solution, cooled by means of an ice-bath. Immediately a white precipitate formed. The solvent was removed and the precipitate filtered and washed repeatedly with cold water. The acid amide formed colorless plates, m.p. 153° (uncor.). The yields were between 70–80% based on the amount of acid used.

Anal. Calcd. for $C_{10}H_{15}ONSi$: Si, 14.5; N, 7.2. Found: Si, 14.8; N, 6.9.

***p*-Trimethylsilylbenzaldehyde** (IV).—To the Grignard solution, made from 62.1 g. of *p*-bromophenyltrimethylsilane, was added a solution of 40.2 g. of ethyl orthoformate in 100 cc. of ether. The mixture was refluxed for 14 hours. It was then ether extracted and the solvent afterwards removed. The residual, brown solid mass was ground up into a fine powder and was slowly added to 750 cc. of a 6% hydrochloric acid solution which was maintained at about 5° by means of an ice-bath. After all the powder had been dissolved it was stirred for four hours and the temperature rose to room temperature. The mixture was ether extracted and the solvent removed. The residual material, representing the acetal (V), was added to 700 cc. of an aqueous solution, containing 100 g. of concd. sulfuric acid. The mixture was refluxed for 15 minutes. Low-boiling material was first removed by distillation. The residual liquid was steam-distilled. The distillate was ether extracted and the solvent afterwards removed. The residual oil crystallized on seeding with a crystal of the aldehyde. The crude yield was 96%. The aldehyde can be purified by recrystallization from ligroin, forming colorless needles, m.p. 109–110° (uncor.). It can also be purified by vacuum distillation, b.p. 119° at 15 mm.

Anal. Calcd. for $C_{10}H_{14}OSi$: Si, 15.73. Found: Si, 15.9.

Infrared analysis showed the presence of carbonyl, phenyl, $Si–CH_3$ and Si–C.

The 2,4-dinitrophenylhydrazone of *p*-trimethylsilylbenzaldehyde formed reddish-orange crystals and recrystallized from alcohol and ethyl acetate melted at 209° (uncor.). The infrared analysis indicated the presence of N–H, $Si–CH_3$, Si–C, $-NO_2$ and phenyl, accounting well for the structure of the 2,4-dinitrophenylhydrazone.

***p*-Bromophenoxytrimethylsilane**.—This compound, previously described by Speier,[2] was prepared from *p*-bromophenol and trimethylchlorosilane using pyridine as hydrohalogen acceptor. The yield was 76–85%.

Anal. Calcd. for $C_9H_{13}OBrSi$: Si, 11.4. Found: Si, 11.3.

***p*-Trimethylsiloxyphenylmagnesium Bromide** (VII).—In a three-necked flask were placed 19 g. of magnesium turnings and 200 cc. of anhyd. ether. A solution of 185 g. of *p*-bromophenoxytrimethylsilane in 200 cc. of ether was gradually added through the dropping funnel. The mixture was then refluxed for 18 hours; 3.8 g. of magnesium was recovered, indicating a 83% yield of the Grignard reagent.

***p*-Trimethylsilylphenoxytrimethylsilane** (VIII).—Half of the above Grignard solution (VII) was slowly added to a solution of 42.7 g. of trimethylchlorosilane in 150 cc. of ether. The mixture was then refluxed for three hours. The inorganic precipitate was filtered off and washed with ether. The ether was removed from the filtrate and the residual liquid fractionated. The product distilled at 114–115° at 20 mm. as a colorless liquid.

Anal. Calcd. for $C_{12}H_{22}OSi_2$: Si, 23.5. Found: Si, 22.0.

The product was slightly impure probably due to contamination by some *p*-bromophenoxytrimethylsilane.

***p*-Trimethylsilylphenol** (IX).—The hydrolysis of the trimethylsiloxy group could not be brought about by mere treatment in dilute acid at room temperature probably due to the insolubility of the compound. Ether extraction of the product, followed by fractionation, resulted in an almost complete recovery of the starting product. The hydrolysis was effected as follows:

10.2 g. of *p*-trimethylsilylphenoxytrimethylsilane (VIII) was added to a solution of 100 cc. of ethanol and 60 cc. of water. The solution was slightly acidified with hydrochloric acid. The mixture was refluxed for one hour, leaving a solid which was recrystallized several times from water, yielding colorless needles, m.p. 74–75° (uncor.). This is in good agreement with the melting point reported by Speier,[2] m.p. 74–74.2°.

Anal. Calcd. for $C_9H_{14}OSi$: Si, 16.9. Found: Si, 16.6.

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Some Reactions of Pentaphenylchlorodisilane

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RECEIVED OCTOBER 6, 1952

The reactions of pentaphenylchlorodisilane have been studied to determine their relationship to those of analogous monosilane compounds, and to test the stability of the Si–Si bond in this hexasubstituted unsymmetrical disilane series.

The reaction of pentaphenylchlorodisilane with primary alcohols proceeds smoothly to give the corresponding pentaphenylalkoxydisilanes. Analogous reactions in the monosilane series have given similar results.[1] Attempts to make the corresponding derivatives of secondary or tertiary alcohols, under conditions used for the preparation of primary alkoxides from pentaphenylchlorodisilane, failed. The preparation of secondary and tertiary alkoxymonosilanes, however, has been reported.[2,3] These results may indicate a characteristic difference between the di- and monosilanes of this type. It is believed that the factor of steric hindrance might be in large part responsible for the anomalous results obtained.

$$(C_6H_5)_3SiSi(C_6H_5)_2Cl + RCH_2OH \longrightarrow (C_6H_5)_3SiSi(C_6H_5)_2OCH_2R + HCl$$

The preparation of pentaphenylhydroxydisilane by the hydrolysis of pentaphenylchlorodisilane

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[1] R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

[2] R. H. Krieble and C. A. Burkhard, *ibid.*, **69**, 2689 (1947); M. N. Kalinin, *Compt. rend. acad. Sci.* (*U.S.S.R.*), **26**, 365 (1940) [*C. A.*, **35**, 2470 (1941)]; C. S. Miner, Jr., L. A. Bryan and R. P. Holysz, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).

[3] Privately communicated studies by Dr. G. N. R. Smart, who has observed some interesting results in reactions between the sterically hindered *o*-Tol_3SiCl and ROH and RONa compounds.