

SYNTHESIS OF *p*-BIS-SILYLARYLENE COMPOUNDS BY THE GRIGNARD REACTION OF *p*-DIBROMOBENZENE WITH DIALKOXY-, DICHLORO-, ALKOXYCHLORO- AND CHLORODIPHENYLSILANES*

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Reactions of *p*-dibromobenzene with diphenyldimethoxysilane, diphenyldiethoxysilane, diphenyldichlorosilane and diphenylchlorosilane gave the corresponding *p*-bromophenyldiphenylsilanes, which, in turn, were used to synthesize unsymmetrical *p*-bis-silylarylene compounds $R^1(C_6H_5)_2SiC_6H_4Si(C_6H_5)_2R^2$, where R^1 and $R^2 = H, OCH_3$ and OC_2H_5 . The function of a bifunctional Grignard agent from *p*-dibromobenzene has been investigated. A new procedure for hydrolysis of *p*-bis-alkoxydiphenylsilylarylene compounds is described.

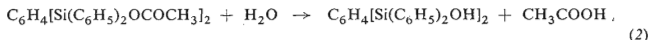
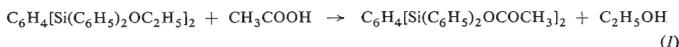
The Grignard reaction is known to be one of the best methods for the synthesis of bis-silylarylene compounds. The use of *p*-dibromobenzene is rewarding owing to its great reactivity to magnesium and to the ready accessibility of the bifunctional Grignard agent, whose reaction with alkoxy- or halosilanes gives rise to the expected *p*-bis-silylarylene compounds. An intermediate are *p*-bromophenylsilanes, formed by the reaction of only one bromine atom of *p*-dibromobenzene. The reaction itself can be accomplished in several ways: A) To a solution of the Grignard agent $BrMg-C_6H_4-MgBr$ an ethereal or tetrahydrofuran solution of the selected silane is added. B) *p*-Dibromobenzene is added to a mixture of magnesium and the silane. C) A solution of *p*-dibromobenzene or *p*-bromophenyldiphenylsilane and the silane is added to magnesium. D) The Grignard agent is added to a solution of the silane. The formation and reactivity of the bifunctional Grignard agent from *p*-dibromobenzene in relation to the solvent and preparative procedure have been studied by a number of authors^{1,2}. The conversion into the bifunctional Grignard agent was found to be greater in tetrahydrofuran than in diethyl ether³.

As a part of our study of *p*-bis-silylarylene compounds we have dealt with the syntheses of symmetrical and unsymmetrical compounds $R^1(C_6H_5)_2SiC_6H_4Si(C_6H_5)_2R^2$, where R^1 and $R^2 = H, OCH_3$ and OC_2H_5 . An intermediate in the reaction of *p*-dibromobenzene with magnesium and a silane $(C_6H_5)_2SiClR^1$ or $(C_6H_5)_2SiR^2$ was the corresponding *p*-bromophenyldiphenylsilane, which was used to synthesize the required unsymmetrical silylarylene compound. The rate of formation of the Grignard agent from *p*-dibromobenzene and magnesium in tetrahydrofuran was determined by gas chromatography from the amount of benzene formed by hydro-

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lysis of samples of the reaction mixture. In this way we also ascertained which of the above-mentioned procedures (A–D) should be selected for a given silane.

An obstacle in the attempted hydrolysis of *p*-bis-diphenylethoxysilylbenzene and unsymmetrical *p*-bis-silylarylene compounds was the poor solubility of these compounds in ethanol, which made it impossible to conduct this reaction in a homogeneous medium at room temperature. The literature^{4–7} describes hydrolysis of bis-alkoxysilylarylene compounds in aqueous alcoholic solutions of NaOH, but our experiments in this medium or in tetrahydrofuran or a benzene–ethanol solution were not successful even at elevated temperatures. It was only hydrolysis in acetic acid containing phosphoric acid and water that proved really effective and produced *p*-bis-diphenylhydroxysilylbenzene in a high yield and satisfactory purity. The essential reactions are the following:



The first step is the formation of a diacetoxy derivative, followed, on the addition of water, by hydrolysis to the corresponding dihydroxy derivative. A by-product is ethyl acetate.

EXPERIMENTAL

Preparation of a Grignard agent from p-dibromobenzene. A flask was charged with *p*-dibromobenzene (23.7 g, 0.1 mol), magnesium shavings (9.7 g, 0.4 mol), nonane (3.9 g) and tetrahydrofuran (100 ml). After activation by 3 drops of bromine the reaction mixture was brought to boil. At selected time intervals samples were withdrawn, decomposed by dilute sulphuric acid and analysed by gas chromatography. After 1, 2 and 6 3/4 h of heating the reaction mixture was found to contain 1.11, 2.05 and 3.35 g of benzene respectively, which implied the formation of 14, 26 and 43% of the bifunctional Grignard agent. In the use of powdered magnesium, the procedure being otherwise the same, we determined 3.01, 3.55 and 4.41 g of benzene, corresponding to the formation of 39, 46 and 57% of the bifunctional Grignard agent, respectively.

Synthesis of p-bromophenyldiphenylsilane. *p*-Dibromobenzene (118.5 g, 0.5 mol) was heated with powdered magnesium (12.2 g) in 500 ml of diethyl ether until all the magnesium was solved. Then diphenylchlorosilane (109.4 g, 0.05 mol) in 250 ml of xylene was added. The temperature of the mixture moderately increased, but on the addition of tetrahydrofuran (50 ml) a vigorous reaction occurred. Xylene (250 ml) was added and the ether was distilled off. The reaction mixture was then refluxed for 3 1/2 h. After cooling and dilution with light petroleum (200 ml) the separated inorganic salts were removed by filtration and washed with benzene. Distillation of the filtrate gave 103.9 g (61%) of *p*-bromophenyldiphenylsilane, b.p. 152–155°C/0.3 Torr. For $\text{C}_{18}\text{H}_{15}\text{BrSi}$ (339.3) calculated: 63.71% C, 4.46% H; found: 63.72% C, 4.51% H.

Synthesis of p-bromophenyldiphenylchlorosilane. A solution of *p*-bromophenylmagnesium bromide, prepared from powdered magnesium (12.1 g) and *p*-dibromobenzene (118.5 g, 0.5 mol)

in 500 ml of diethyl ether, was slowly added dropwise and under stirring to a solution of diphenyldichlorosilane (126.6 g, 0.5 mol) in 300 ml of tetrahydrofuran. The reaction mixture was refluxed for 1 h, then the solvents were distilled off until the temperature of the distilling vapour had attained 78°C. The mixture was refluxed for 1 more hour, cooled and diluted with 1 l of light petroleum. The separated salts were removed by filtration and washed with benzene. Distillation of the filtrate gave 65.4 g (35%) of the product, b.p. 170–180°C/0.7 Torr, m.p. 43–45°C; the reported⁸ b.p. is 178–188°C/0.25 Torr.

Synthesis of p-bromophenyldiphenylethoxysilane. To a solution of *p*-bromophenylmagnesium bromide, prepared from magnesium shavings (12.1 g) and *p*-dibromobenzene (118.5 g, 0.5 mol) in 500 ml of diethyl ether, was added a solution of diphenylethoxychlorosilane (131.3 g, 0.5 mol) in 300 ml of xylene. The temperature of the mixture just moderately rose, but on the addition of 50 ml of tetrahydrofuran a vigorous exothermic reaction occurred. The ether was distilled off, while 200 ml of xylene was added. The reaction mixture was refluxed for 3 1/2 h, cooled, diluted with light petroleum and filtered to remove the separated salts, which were washed with benzene. Distillation gave 130.0 g (68%) of the product, b.p. 180–190°C/1.8 Torr, m.p. 42.5–43.0°C (ethanol). For C₂₀H₁₉BrOSi (383.34) calculated: 62.66% C, 5.00% H; found: 62.52% C, 4.99% H.

Synthesis of p-bromophenyldiphenylmethoxysilane. The procedure was the same as that for the ethoxy derivative, yield 60%, b.p. 168–170°C/0.5–0.6 Torr, m.p. 54–55°C (methanol). For C₁₉H₁₇BrOSi (369.31) calculated: 61.79% C, 4.64% H; found: 61.68% C, 4.68% H.

Synthesis of p-bis-diphenylsilylbenzene. A mixture of *p*-dibromobenzene (23.7 g, 0.1 mol) and magnesium shavings (7.3 g, 0.3 mol) in 100 ml of tetrahydrofuran was activated by 3 drops of bromine and heated to the boiling temperature. The reaction started in 15 min. The mixture was refluxed for 6 1/2 h and cooled. After the addition of diphenylchlorosilane (43.74 g, 0.2 mol) it spontaneously heated and yellow-to-green salts separated, which went back to solution in 5 min. The reaction mixture was refluxed for 3 h, then 25.3 g of an 80% benzene solution of sodium bis-(2-methoxyethoxy)aluminium hydride (0.1 mol) was added and the mixture was refluxed for 30 min. After cooling the reaction mixture was decomposed by 20% sulphuric acid and worked up in the usual manner. Distillation gave the following fractions, b.p. up to 60°C/0.5 Torr (6.4 g), b.p. 106–110°C/0.2 Torr (4.9 g), b.p. 215–220°C/0.2–0.3 Torr (26.4 g). The distillate melted at 97–100°C, after crystallization from petrol the m.p. was 103.5–105°C and after recrystallization from acetone it was 105–107°C. The total yield of *p*-bis-diphenyl silylbenzene was 59.6%. The reported melting points and yields are 83°C, 52% (ref.⁹); 95°C, 49% (ref.¹⁰); 102–105°C, 39% (ref.⁶) and 107–108°C, 47% (ref.⁷).

Synthesis of p-bis-diphenylethoxysilylbenzene. The Grignard agent was prepared from *p*-dibromobenzene (47.2 g, 0.2 mol) and magnesium shavings (10.7 g) in 250 ml of tetrahydrofuran + 3 drops of bromine. The mixture was refluxed for 7 h. Diphenyldiethoxysilane (188.85 g, 0.4 mol) was added to the cooled mixture, which was then refluxed for 3 more hours. A portion of tetrahydrofuran was distilled off under reduced pressure and 300 ml of light petroleum was added. The separated salts were removed by filtration and washed with warm light petroleum. The filtrate was composed of a brown oily liquid and a layer of the light petroleum solution. The latter was concentrated under reduced pressure. The separated crystalline portion was dissolved in a little benzene and 500 ml of boiling ethanol was added. After cooling there separated 12.84 g (12.1%) of the product, m.p. 163–164°C. The reported⁶ m.p. and yield are 158–161°C, 28%. The brown oil was also taken into a small amount of benzene, then 250 ml of boiling ethanol was added. After cooling to –20°C 6.9 g of inorganic salts separated.

Synthesis of 1-diphenylethoxysilyl-4-diphenylsilylbenzene. To a flask containing powdered magnesium (2.43 g, 0.1 mol) activated by a drop of bromine was added in the course of 20 min

a solution of *p*-bromophenyldiphenylethoxysilane (19.17 g, 0.05 mol) and diphenylchlorosilane (10.95 g, 0.05 mol) in 50 ml of tetrahydrofuran. The reaction mixture was refluxed for 4 h, cooled and diluted with light petroleum. The separated inorganic salts were removed by filtration and washed with benzene. The filtrate was concentrated under reduced pressure and the distillation residue was taken into hot benzene. The inorganic salts were filtered off and the benzene solution was concentrated. Crystallization of the residue from petrol (b. p. 90–110°C) yielded a compound melting at 190–205°C (0.4 g) and the product melting at 83–86°C (11.8 g, 49%). After another crystallization from petrol or ethanol the m.p. was 86–86.5°C. For $C_{32}H_{30}OSi_2$ (486.7) calculated: 78.97% C, 6.21% H; found: 79.16% C, 6.32% H.

Synthesis of 1-diphenylmethoxysilyl-4-diphenylsilylbenzene. To powdered magnesium (2.67 g, 0.11 mol) was added in the course of 35 min a solution of *p*-bromophenyldiphenylsilane (33.93 g, 0.1 mol) in 50 ml of tetrahydrofuran + 2 drops of the 80% benzene solution of $NaAlH_2 \cdot (OCH_2CH_2OCH_3)_2$. The reaction mixture was refluxed for 30 min, then a solution of diphenylmethoxychlorosilane (24.88 g, 0.1 mol) in 40 ml of tetrahydrofuran was added in the course of 15 min. The reaction mixture was kept boiling 4 h, 50 ml of the solvent being distilled off. After cooling the reaction mixture was diluted with light petroleum and the separated salts were filtered off and washed with benzene. The solvents were removed from the filtrate under reduced pressure and the residue was crystallized from methanol, yield 35.0 g (74%) of the product, m.p. 98–103°C. Recrystallization raised the m.p. to 109–110°C. For $C_{31}H_{28}OSi_2$ (472.7) calculated: 78.76% C, 5.97% H; found: 78.94% C, 5.86% H.

Synthesis of 1-diphenylmethoxysilyl-4-diphenylethoxysilylbenzene. To powdered magnesium (3.90 g) in 20 ml of tetrahydrofuran was added during 30 min a solution of *p*-bromophenyldiphenylmethoxysilane (29.55 g, 0.08 mol) and diphenylethoxychlorosilane (21.0 g, 0.08 mol) in 50 ml of tetrahydrofuran + 2 drops of the benzene solution of $NaAlH_2 \cdot (OCH_2CH_2OCH_3)_2$. The reaction mixture was refluxed for 5 1/2 h, then it was diluted with light petroleum. The separated inorganic salts were filtered off and washed with benzene. The filtrate was taken to dryness under reduced pressure. The dry residue was boiled in benzene. The inorganic salts were filtered off and washed with benzene. The filtrate was again taken to dryness. Crystallization of the residue from petrol gave 18.0 g (44%) of the product, m.p. 130–135°C. On recrystallization the m.p. increased to 136–137.5°C. For $C_{33}H_{32}O_2Si_2$ (500.8) calculated: 76.70% C, 6.24% H; found: 77.06% C, 6.13% H.

Alkaline hydrolysis of p-bis-diphenylethoxysilylbenzene. To a solution of 5.75 g of sodium in 35 ml of methanol and 8.5 ml of water was added 25 ml of ethanol and 26.5 g of the diethoxysilyl derivative. After 1 hour's standing the suspension was boiled for 5 min, then it was diluted with 10 g of NaOH in 39 ml of water. After an hour's stirring the insoluble portion was filtered off and washed with ethanol; its m.p. identified it as the unreacted starting compound. The filtrate was acidified with phosphoric acid. The separated solid was dried and twice crystallized from toluene, m.p. 224–225°C. The reported m.p. 212–214°C (ref.¹¹), 216–217°C (ref.⁵), 219°C (ref.¹²), 224–226°C (ref.⁶) and 226–228°C (ref.⁷). The total yield of the dihydroxy derivative was 2.7 g (11.5%).

Acid hydrolysis of p-bis-diphenylethoxysilylbenzene. *p*-Bis-diphenylethoxysilylbenzene (361 g) was dissolved by heating in 632 g of glacial acetic acid containing 4.8 g of 80% phosphoric acid. After 10 minutes' boiling 200 ml of boiling water was added. The solution was allowed to cool down and left standing overnight. The separated dihydroxy derivative was collected on a filter, washed with water and allowed to get dry in the air; yield 316.5 g (98.3%), m.p. 222–223°C. From the filtrate combined with the washing water was obtained another 1.9 g (0.6%) of the product, m.p. 220–222°C.

Hydrolysis of 1-diphenylmethoxysilyl-4-diphenylethoxysilylbenzene. One g of this compound was hydrolysed by boiling in 25 ml of glacial acetic acid containing 5 drops of 85% phosphoric acid for 5 min. After the addition of 5 ml of hot water and cooling the separated *p*-bis-diphenylhydroxysilylbenzene was collected on a filter, washed with water and crystallized from toluene, m.p. 221–222°C.

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