

SYNTHESIS OF *p*-CHLOROPHENYLDIPHENYLSILANES AND UNSYMMETRICAL *p*-BIS-SILYLARYLENES FROM *p*-DICHLOROBENZENE AND *p*-BROMOCHLOROBENZENE BY THE GRIGNARD REACTION*

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Reactions of *p*-dichlorobenzene and *p*-bromochlorobenzene with diphenylchloro-, diphenylethoxychloro-, diphenyldichloro- and diphenyldimethoxysilane gave compounds $p\text{-ClC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{R}^1$. From these were synthesized unsymmetrical *p*-bis-silylarylenes $\text{R}^1(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{R}^2$, where R^1 and $\text{R}^2 = \text{Cl, H, OCH}_3$ and OC_2H_5 . The formation of a bifunctional Grignard agent from *p*-dichlorobenzene has been investigated.

In the synthesis of symmetrical *p*-bis-silylarylenes $\text{R}^1(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{R}^1$, where $\text{R}^1 = \text{Cl, H, OCH}_3$ or OC_2H_5 , from *p*-dibromobenzene or *p*-dichlorobenzene by the Grignard reaction there are also formed $p\text{-ClC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{R}^1$ and $p\text{-BrC}_6\text{H}_4(\text{C}_6\text{H}_5)_2\text{R}^1$. In the case of *p*-dibromobenzene the reaction conditions and the ratio of the starting components can be so selected that either a mono or a disilyl compound is the main product¹. The use of *p*-bromochlorobenzene for the synthesis of bis-silyl compounds is very limited by an insufficient reactivity of the chlorine atom to magnesium, so that reactions with trimethylchlorosilane², diphenyldichlorosilane³ or diphenyldiethoxysilane⁴ afforded only the respective monosilyl derivatives, *i.e.* $p\text{-ClC}_6\text{H}_4\text{Si}(\text{CH}_3)_3$, $p\text{-ClC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}$ and $p\text{-ClC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)$. In the use of *o*-dichlorobenzene the yields of the reactions with trimethylchlorosilane⁵ or silanes $(\text{C}_6\text{H}_5)_2\text{SiR}^1\text{R}^2$ were raised⁶ to as high as 88% by employing toluene or xylene as the reaction medium. Where monosilyl derivatives were desired the reaction of *p*-dichlorobenzene with trimethylchloro- or dimethyldichlorosilane gave the corresponding *p*-chlorophenylsilanes in a 33% (ref.⁵) and 30% (ref.⁷) yield.

This paper describes the synthesis of compounds $p\text{-ClC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{R}^1$, which are by-products from the preparation of symmetrical *p*-bis-silylarylenes and can be employed as starting compounds for the synthesis of the unsymmetrical compounds $\text{R}^1(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{R}^2$. The formation of the bifunctional Grignard agent $\text{ClMgC}_6\text{H}_4\text{MgCl}$ by reaction of *p*-dichlorobenzene with activated magnesium in tetrahydrofuran is also dealt with. *p*-Chlorophenyldiphenylsilane, *p*-chlorophenyldiphenylmethoxysilane and the corresponding ethoxy derivative were prepared in

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good yields from *p*-chlorophenyldiphenylchlorosilane by its reactions with $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$, methanol or ethanol. Unsymmetrical *p*-bis-silylarylenes were obtained by a judicious combination of the starting silanes. Thus the reaction of *p*-chlorophenyldiphenylethoxysilane with diphenylchlorosilane gave $(\text{C}_2\text{H}_5\text{O}) \cdot (\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2\text{H}$, and the reaction of *p*-chlorophenyldiphenylmethoxysilane with diphenylethoxychlorosilane gave $(\text{C}_2\text{H}_5\text{O})(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4(\text{C}_6\text{H}_5)_2(\text{OCH}_3)$.

We have also investigated the formation of the Grignard agent from *p*-dichlorobenzene in tetrahydrofuran. This was followed as in the case of *p*-dibromobenzene¹: an aliquot portion of the reaction mixture was hydrolysed and the quantity of benzene was determined by gas chromatography with the aid of an internal standard; this quantity corresponded to the amount of $\text{ClMgC}_6\text{H}_4\text{MgCl}$ in the reaction mixture. The magnesium employed had been activated by a tenth of the stoichiometric amount of *p*-dibromobenzene and when the reaction had started a solution of *p*-dichlorobenzene in tetrahydrofuran was slowly added. In the use of magnesium shavings there were found after 1, 3, 5 and 10 hour' heating 6, 7, 7 and 9% of benzene, respectively, whereas with powdered magnesium 11, 11, 10 and 9% of benzene. In considering these values it must be borne in mind that the starting reaction mixture contained 9.1% of *p*-dibromobenzene and 90.9% of *p*-dichlorobenzene, so that as much as 9.1% of benzene may have arisen from the dibromo derivative and only the amounts above this level can be ascribed to the *p*-dichloro derivative.

Diphenylchlorosilane, used in the reactions, can be obtained either by partial reduction of the dichloro derivative or by chlorination of diphenylsilane. In the former case the reduction was effected by LiBH_4 (ref.⁸) or by $\text{NaBH}_4 + \text{NaH}$ in the presence of esters⁹; the yields were low, 60% and 42% respectively. A more rewarding method is the direct chlorination of diphenylsilane¹⁰, which can be obtained by reduction of diphenyldichlorosilane with LiAlH_4 (ref.¹¹) or Na_3AlH_6 (ref.¹²) the yields being 75.6 and 61% respectively. In our work diphenyldichlorosilane was reduced with $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ to diphenylsilane in an 88% yield. It has been ascertained that even in the inverse method of the reduction under cooling this hydride fails to reduce the dichloro derivative partially to the monochloro derivative.

EXPERIMENTAL

Synthesis of p-chlorophenyldiphenylchlorosilane. To a stirred solution of diphenyldichlorosilane (63.3 g, 0.25 mol) in 100 ml of tetrahydrofuran a solution of the Grignard agent prepared from *p*-bromochlorobenzene (47.8 g, 0.25 mol) in 100 ml of tetrahydrofuran and magnesium shavings (6.1 g) was added in the course of 1 h. The reaction mixture was refluxed for 22 h. Most of the solvent was then removed by distillation *in vacuo* and the inorganic salts were separated by the addition of benzene. Distillation gave *p*-chlorophenyldiphenylchlorosilane (52.15 g, 63%), b.p. 167–170°C/0.65 Torr, m.p. 27–28°C (the reported³ b.p. is 149–150°C/0.3 Torr, yield 36%).

When the solution of the Grignard agent was added dropwise to a solution of diphenyldichlorosilane in 200 ml of xylene and after distilling off tetrahydrofuran the mixture was refluxed for 3 1/2 h only there was obtained 62% of chlorosilane.

Synthesis of p-chlorophenyldiphenylsilane. Procedure A. A flask was charged with powdered magnesium (6.7 g, 0.275 mol), *p*-bromochlorobenzene (4.8 g, 0.025 mol) and 100 ml of tetrahydrofuran containing 3 drops of an 80% benzene solution of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$. After activation by bromine and the start of the reaction a solution of *p*-dichlorobenzene (36.75 g, 0.25 mol) and diphenylchlorosilane (60.2 g, 0.275 mol) in 300 ml of xylene was added in the course of 1 h. The reaction mixture was then boiled for 6 h, during which time 95 ml of tetrahydrofuran distilled off. After cooling the reaction mixture was diluted with light petroleum and the separated salts were removed by filtration. Distillation of the filtrate gave 26.3 g (34%) of *p*-chlorophenyldiphenylsilane boiling at 132–142°C/0.3 Torr; the reported³ b.p. is 161–162°C/1 Torr. Procedure B: *p*-Chlorophenyldiphenylchlorosilane (10.9 g) in benzene was reduced by boiling with 11.5 g of an 80% benzene solution of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ for 30 min; yield 8.0 g (77%) of *p*-chlorophenyldiphenylsilane, b.p. 129–130°C/0.1 Torr. In the literature³ the reducing agent was LiAlH_4 and the yield was 56%.

Synthesis of p-chlorophenyldiphenylethoxysilane. Procedure A: To magnesium shavings (6.1 g) was added dropwise under stirring a solution of *p*-bromochlorobenzene (47.8 g, 0.25 mol) in 100 ml of tetrahydrofuran containing 3 drops of the 80% benzene solution of the hydride. The reaction mixture was kept at the boiling temperature for 2 h, in which time all the magnesium had dissolved. The solution of *p*-chlorophenylmagnesium bromide was added in the course of 50 min to a solution of diphenylethoxychlorosilane (65.4 g, 0.25 mol) in 200 ml of xylene. The reaction mixture was boiled for 3 1/2 h, in which time 90 ml of tetrahydrofuran distilled off. The cooled reaction mixture was diluted with light petroleum and the separated salts were removed by filtration. Distillation of the filtrate gave 55.45 g (64%) of *p*-chlorophenyldiphenylethoxysilane boiling at 175–180°C/0.7 Torr. Procedure B: A mixture of pyridine (9.6 g), absolute ethanol (6.5 g) and benzene (50 ml) was cooled to 0°C and *p*-chlorophenyldiphenylchlorosilane (18.1 g, 0.055 mol) in 50 ml of benzene was added under stirring in the course of 30 min. The reaction mixture was stirred 4 h and left standing overnight. The salts were removed by filtration and washed with benzene. The filtrate and the washings were combined and concentrated. There separated another portion of salts which went back to the solution on the addition of water. The product was taken into benzene, yield 9.85 (53%) of *p*-chlorophenyldiphenylethoxysilane, b.p. 130–136°C/0.1 Torr. Procedure C: A flask was charged with powdered magnesium (7.13 g, 0.293 mol), *p*-bromochlorobenzene (4.79 g, 0.025 mol), tetrahydrofuran (100 ml) and 3 drops of the 80% hydride in benzene. After activation by a few drops of bromine and the start of the reaction a solution of *p*-dichlorobenzene (36.75 g, 0.25 mol) and diphenylethoxychlorobenzene (72.19 g, 0.275 mol) in 300 ml of xylene was added in the course of 1 h under stirring. The reaction mixture was boiled 4 1/4 h, in which time the boiling temperature rose to 130°C and 90 ml of the solvents had distilled off. After cooling the reaction mixture was diluted with light petroleum and the separated salts were removed by filtration. The filtrate was distilled, the fraction 158–168°C/0.3–0.4 Torr being collected as the product, yield 53.75 g (58%). The products obtained in procedures A, B and C were combined and redistilled; yield 113.3 g of a fraction boiling at 148–154°C/0.2 Torr, m.p. 31.0–32.5°C. The reported⁴ b.p. is 158–160°C/0.25 Torr.

Synthesis of p-chlorophenyldiphenylmethoxysilane. Procedure A.: This was analogous to procedure C in the case of the ethoxy derivative, except that the reaction mixture was refluxed for 6 h, yield 54% of a product collected at 138–142°C/0.2–0.3 Torr, m.p. 41.0–41.5°C (methanol). For $\text{C}_{19}\text{H}_{17}\text{ClOSi}$ (324.9) calculated: 70.24% C, 5.27% H; found: 69.99% C, 5.33% H. Procedure B: *p*-chlorophenyldiphenylchlorosilane (4.0 g, 0.0122 mol) was dissolved in light petroleum (5 ml),

then dried methanol (4.3 g, 0.0134 mol) was added. The reaction mixture was boiled 15 min. Distillation gave *p*-chlorophenyldiphenylmethoxysilane, b.p. 148–152°C/0.5 Torr, m.p. 41.5 to 42.0°C.

Synthesis of 1-diphenylethoxysilyl-4-diphenylsilylbenzene. A flask was charged with powdered magnesium (5.35 g) and *p*-bromophenyldiphenylethoxysilane (3.8 g, 0.01 mol) in 40 ml of tetrahydrofuran. After activation by bromine and the start of the reaction a solution of *p*-chlorophenyldiphenylethoxysilane (33.85 g, 0.1 mol) and diphenylchlorosilane (24.0 g, 0.11 mol) in 100 ml of xylene was added during 30 min. When 45 ml of the solvents had distilled off the reaction mixture was refluxed 5 h, then cooled and diluted with light petroleum. The separated salts were removed by filtration and washed with benzene. The solvents were removed by distillation *in vacuo*. The residue was crystallized from petrol. There first separated 2.3 g of a substance melting at 196–210°C. After concentration of the remaining liquor there was further obtained 1-diphenylethoxysilyl-4-diphenylsilylbenzene (26.2 g, 49%), m.p. 83–85°C, undepressed on admixture of the product obtained from *p*-bromophenyldiphenyl-ethoxysilane¹, m.p. 86.0–86.5°C.

Synthesis of 1-diphenylmethoxysilyl-4-diphenylethoxysilylbenzene. *p*-Bromophenyldiphenylmethoxysilane (0.01 mol), *p*-chlorophenyldiphenylmethoxysilane (0.1 mol) and diphenylethoxysilylchlorosilane (0.11 mol) were reacted in the same way; yield 37.4 g (66%) of the crude product. After crystallization from petrol its m.p. 134–135°C was not depressed on admixture of a preparation melting at 136–137.5°C, which had been obtained from *p*-bromophenyldiphenylmethoxysilane¹.

Reduction of diphenyldichlorosilane by NaAlH₂(OCH₂CH₂OCH₃)₂. The course of the reduction, conducted in benzene, was followed by gas chromatography. A 250-ml flask was charged with diphenyldichlorosilane (25.3 g, 0.1 mol) in 100 ml of benzene under an atmosphere of nitrogen, and a solution of the hydride in benzene was slowly added under cooling to 0°C. The reaction immediately produced diphenylsilane, which was found beside the unreacted diphenyldichlorosilane. When 0.11 mol of the hydride had been added no unreacted diphenyldichlorosilane was left in the reaction mixture. Diphenylsilane was prepared by the addition of diphenyldichlorosilane (126.6 g, 0.5 mol) to a mixture of a benzene solution of the hydride (158 g of a 70% solution, 0.55 mol) and 400 ml of absolute benzene. The reaction mixture was boiled for 20 min and worked up in the usual manner; yield 80.8 g (88%), b.p. 126–127°C/12 Torr.

Preparation of a Grignard agent from p-dichlorobenzene. A mixture of *p*-dibromobenzene (2.37 g, 0.01 mol) and fine magnesium shavings (10.7 g, 0.44 mol) in 50 ml of tetrahydrofuran was activated by 3 drops of bromine. When the reaction had started *p*-dichlorobenzene (14.70 g, 0.1 mol) and nonane (4.3 g) in 60 ml of tetrahydrofuran were added and the reaction mixture was brought to the boiling temperature. Samples were taken at selected intervals, decomposed by 20% sulphuric acid and analysed by gas chromatography.

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