

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

† V. BAŽANT and M. ČERNÝ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchbát*

Received August 30th, 1973

Employing activated magnesium, the Grignard reaction *in situ* of *p*-dichlorobenzene with dichloro-, chloro-, dimethoxy-, diethoxy-, ethoxychloro- and methoxychloro-diphenylsilanes in tetrahydrofuran, toluene, or xylene gave high yields of the expected *p*-bis-diphenylsilylbenzenes.

p-Bis(diphenylhydroxysilyl)benzene, $(C_6H_5)_2(OH)SiC_6H_4Si(OH)(C_6H_5)_2$, is the main source for the synthesis of binary silylarylene resins^{1,2}. From the economic point of view it appears rewarding to synthesize this compound by the Grignard reaction from *p*-dichlorobenzene and diphenyldichlorosilane as accessible products. As is known, however, *p*-dichlorobenzene does not react with magnesium in ether to form a Grignard agent. The reaction proceeds in tetrahydrofuran as solvent; the monofunctional Grignard agent ClC_6H_4MgCl was obtained in 76% (ref.³), 90% (ref.^{4,5}) and 96% (ref.⁶) yields, the bifunctional agent in 91% (ref.⁷) and 107% (ref.⁸) yields. However, the practical utility of these agents, prepared in such high yields, is limited by low yields of the corresponding *p*-bis-silylarylene compounds, formed by the reaction of the bifunctional Grignard agent with silanes containing two reactive groups⁹. In experiments with silanes having only one reactive group, *e.g.* $(CH_3)_3SiCl$, the bis-silylarylene compound $(CH_3)_3SiC_6H_4Si(CH_3)_3$ was prepared¹⁰ in an 84% yield. In the case of methyl-diethoxychlorosilane, as a silane with three reactive groups, the reaction of only one chlorine atom of *p*-dichlorobenzene gave the corresponding product $p-ClC_6H_4SiCH_3(OC_2H_5)_2$ in a 32% yield¹¹. Similarly, in the reaction of *p*-bromochlorobenzene with trimethylchlorosilane or diphenyldichlorosilane only the bromine atom reacted with magnesium with the formation of the corresponding monosilylarylene, *i.e.* $ClC_6H_4\cdot Si(CH_3)_3$ (ref.¹²) or $ClC_6H_4SiCl(C_6H_5)_2$ (ref.¹³).

Since even in the use of powdered activated magnesium *p*-dichlorobenzene in tetrahydrofuran failed to give a satisfactory yield of the bifunctional Grignard agent, we conducted the Grignard reaction *in situ*: a solution of dihaloarylene and silane was slowly added to activated magnesium. Attention was paid to the effects of the reaction time, temperature, solvent and form of magnesium on the yield of the corresponding *p*-bis-silylarylene compound. In the reaction of *p*-dichlorobenzene and diphenylchlorosilane with activated magnesium in the form of shavings and/or powder

* Part CXV in the series Organosilicon Compounds; Part CXIV: This Journal 39, 1313 (1974).

in tetrahydrofuran the yields of *p*'-bis(diphenylsilyl)benzene were 62 and 69%, respectively. In order that the unreacted diphenylchlorosilane would not interfere with the working up of the reaction mixture (to prevent its hydrolysis on the addition of water to the reaction mixture and to prevent the formation of undesirable products), all the active chlorine atoms on silicon were reduced by the addition of $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2)_2$. The by-products were *p*-chlorophenyldiphenylsilane and triphenylsilane, the latter was formed as a result of the reductive displacement of the chlorine atom bound to the benzene ring. Reaction of *p*-dichlorobenzene with diphenyldichlorosilane and magnesium in tetrahydrofuran gave a mixture difficult to work up, because of the reactive chlorine on the silicon atom. To be sure that the desired product was present the reaction mixture was treated with $\text{NaAlH}_2(\text{OCH}_2\text{CH}_2)_2$, whereupon distillation gave *p*-bis(diphenylsilyl)benzene. The detected by-products were *p*-chlorophenyldiphenylsilane and triphenylsilane. For comparison we also employed magnesium in the forms of powder and shavings but in neither case was the result satisfactory.

In the reaction of *p*-dichlorobenzene with diphenyldimethoxysilane we investigated the effects of solvent (its boiling temperature) and the form of magnesium upon the yield of *p*-bis(diphenylmethoxysilyl)benzene. The results are summarized in Table I; they show that the powdered form of magnesium and an elevated temperature raise the yield. The structure of the hitherto undescribed *p*-bis(diphenylmethoxysilyl)benzene was confirmed by its conversion into the previously described *p*-bis(diphenylhydroxysilyl)benzene.

In the reaction of *p*-dichlorobenzene with diphenyldiethoxysilane and activated magnesium the yield of *p*-bis(diphenylethoxysilyl)benzene was increased to as much

TABLE I
Reactions of *p*-Dichlorobenzene with Halo- and Alkoxyasilanes

Silane	Product	Solvent	Yield	
			% ^a	% ^b
$(\text{C}_6\text{H}_5)_2\text{SiHCl}$	$(\text{C}_6\text{H}_5)_2\text{HSiC}_6\text{H}_4\text{SiH}(\text{C}_6\text{H}_5)_2$	THF ^c	62	69
		THF	6	18
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OCH}_3)_2$	$(\text{CH}_3\text{O})(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2(\text{OCH}_3)$	toluene	25	27
		xylene	30	66
$(\text{C}_6\text{H}_5)_2\text{SiCl}(\text{OCH}_3)$	$(\text{CH}_3\text{O})(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2(\text{OCH}_3)$	xylene	—	80
		THF	13	32
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OC}_2\text{H}_5)_2$	$(\text{C}_2\text{H}_5\text{O})(\text{C}_6\text{H}_5)_2\text{SiC}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_2(\text{OC}_2\text{H}_5)$	toluene	15	58
		xylene	15	59

^a Magnesium shavings, ^b magnesium powder, ^c THF — tetrahydrofuran.

as 58% by the use of powdered magnesium and a suitable solvent (Table I). Although Table I clearly demonstrates the favourable effects of the powdered form of magnesium and temperature, no appreciable difference in yield was observed between boiling toluene and xylene as solvents. The by-products detected beside the unreacted diphenyldiethoxysilane were *p*-chlorophenyldiphenylethoxysilane and triphenylethoxysilane.

The reaction of *p*-dichlorobenzene with diphenylethoxychlorosilane and magnesium activated by *p*-dibromobenzene has been explored in more detail. We investigated the effects of temperature (*i.e.* boiling point of the solvent), the form of magnesium and its excess, amount of *p*-dibromobenzene necessary for the activation of magnesium, mode of working up of the reaction mixture and isolation of the products, and the way of drying the solvents. Table II gives the yields of *p*-bis(diphenylethoxysilyl)benzene and *p*-bis(diphenylhydroxysilyl)benzene under different reaction conditions; the effect of temperature is clearly apparent. Also evident are the differences in yield due to the form of magnesium: powder, fine shavings, coarse shavings. If the magnesium was not activated by *p*-dibromobenzene in tetrahydrofuran, or if the activation was attempted in diethyl ether, the main reaction failed to occur and the starting compounds were isolated from the reaction mixture.

The solvents were dried by distillation with sodium bis-2-methoxyethoxyaluminium hydride in pre-annealed flasks. The anhydrous solvents (xylene or tetrahydrofuran) had to be used soon, otherwise the reaction failed to occur or the yields were low. After this observation we found it useful to add a small amount of the hydride to the solvents or the reaction mixture. The loss in yield caused by the reaction of the hydride with diphenylethoxychlorosilane was smaller than that caused by a trace of moisture in the solvent.

Table II further shows the marked effect of the form of magnesium on the yield of the diethoxy derivative. In the use of powdered magnesium instead of magnesium in the form of fine shavings the yields increased from 52 to 61% in tetrahydrofuran as solvent, from 74 to 76% in toluene, and from 78 to 88% in xylene. Magnesium in the form of coarse shavings reduced the yield to 45%. The amount of *p*-dibromobenzene for the activation of magnesium was a tenth or twentieth of the amount of dichlorobenzene. Attempts at activation of magnesium by ethylene dibromide were not successful; no diethoxy derivative was isolated from the reaction mixture.

In working up the reaction mixture the inorganic salts were removed by precipitation on the addition of light petroleum. The light petroleum was removed from the filtrate by distillation and the residue was triturated with ethanol. The crude *p*-bis(diphenylethoxysilyl)benzene thus obtained was in some cases purified by crystallization. In three experiments the distillation residue was directly hydrolysed to *p*-bis(diphenylhydroxysilyl)benzene, which was isolated. In view of the high yields of the dihydroxy derivative in hydrolysis¹⁴ these differences had no importance for judging the courses of these reactions.

To complement the survey of syntheses of *p*-bis-silylarylene compounds, *p*-dichlorobenzene was reacted with diphenylmethoxychlorosilane and activated magnesium in xylene; the yield of *p*-bis(diphenylmethoxysilyl)benzene was 80%.

TABLE II

Yield of *p*-Bis(diphenylethoxysilyl)benzene in the Reaction of *p*-Dichlorobenzene with Diphenylethoxychlorosilane

Solvent	Form of Mg	Excess of Mg %	Yield		
			% ^a	% ^b	% ^c
Tetrahydrofuran	fine shavings	100	52	—	—
	powder	100	61	—	—
Toluene	fine shavings	100	74	—	—
	powder	100	76	—	—
Xylene	coarse shavings	100	—	—	45
	fine shavings	100	78	—	—
	powder	100	88	93	—
		50	85	86	82
		24	—	77	—
		20	—	—	61
		10	61	—	—

^a Reaction of 0.1 mol $\text{ClC}_6\text{H}_4\text{Cl}$ + 0.01 mol $\text{BrC}_6\text{H}_4\text{Br}$ + 0.22 mol $(\text{C}_6\text{H}_5)_2\text{SiCl}(\text{OC}_2\text{H}_5)$.

^b Yields of *p*-bis(diphenylhydroxysilyl)benzene. ^c Reaction of 0.1 mol $\text{ClC}_6\text{H}_4\text{Cl}$ + 0.005 mol $\text{BrC}_6\text{H}_4\text{Br}$ + 0.21 mol $(\text{C}_6\text{H}_5)_2\text{SiCl}(\text{OC}_2\text{H}_5)$.

EXPERIMENTAL

Reaction of p-dichlorobenzene with diphenylchlorosilane. Magnesium shavings (10.7 g, 0.44 mol) and *p*-dibromobenzene (2.37 g, 0.01 mol) in 50 ml of tetrahydrofuran were treated with 3 drops of bromine; the mixture was warmed and after 20 min the reaction started. Following the activation a solution of *p*-dichlorobenzene (14.7 g, 0.1 mol) and diphenylchlorosilane (53.7 g, 0.246 mol) in 60 ml of tetrahydrofuran was added in the course of 1 h under stirring. The reaction mixture was refluxed 4 1/2 h and after the addition of 31 g of an 80% benzene solution of $\text{NaAlH}_2 \cdot (\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ it was boiled for another 30 min. The reaction mixture was then cooled, decomposed with 20% sulphuric acid and worked up in the usual way. Distillation gave the following fractions: b.p. 65–100°C/0.2 Torr, 4.0 g (predominantly diphenylsilane); 116–150°C/0.2 Torr, 5.05 g (66% of triphenylsilane, 30% of *p*-chlorophenyldiphenylsilane and 4% of unidentified products); b.p. 195–210°C/0.2 Torr, 30.37 g (62.3%) of *p*-bis(diphenylsilyl)benzene. After one crystallization from light petroleum the last fraction gave a product melting at 103–105°C. In the case of powdered magnesium the procedure and the ratio of the reaction components were the same. After activation by bromine the reaction started even in the cold; yield 33.65 g

(69%). Reported: m.p. 102–105°C, yield 39% (ref.¹⁵); 107–108°C, 47% (ref.¹⁶); 105–107°C, 60% (ref.¹⁴).

Reaction of p-dichlorobenzene with diphenyldichlorosilane. The procedure was the same as in the foregoing reaction except that a twofold amount of the hydride was employed. With magnesium shavings the fractions were: b.p. 70–80°C/0.2 Torr, 10.00 g (predominantly diphenylsilane; b.p. 110–128°C/0.2 Torr, 9.10 g (41% triphenylsilane, 49% *p*-chlorophenyldiphenylsilane and 10% unidentified compounds); b.p. 140–160°C/0.3 Torr, 1.73 g (12% triphenylsilane, 83% *p*-chlorophenyldiphenylsilane, 5% unidentified); b.p. 207–230°C/0.3 Torr, 10.03 g (21%) of *p*-bis(diphenylsilyl)benzene. The distillation residue was 19.9 g. In the use of powdered magnesium the yield of the crude *p*-bis(diphenylsilyl)benzene was 4.04 g (8.3%). The fractions were analysed by gas chromatography on earthenware coated with 3% of silicone elastomer or on chromosob W coated with 7% of Apiezon W; an apparatus with heat-conductance detection was employed.

Reaction of p-dichlorobenzene with diphenyldimethoxysilane in tetrahydrofuran. To magnesium shavings (10.7 g, 0.44 mol) was added *p*-dibromobenzene (2.37 g, 0.01 mol) and 50 ml of tetrahydrofuran. After activation by 3 drops of bromine and heating the reaction started in 15 min. Then a solution of *p*-dichlorobenzene (14.7 g, 0.1 mol) and diphenyldimethoxysilane (53.7 g, 0.22 mol) in 60 ml of tetrahydrofuran was added in the course of 2 h. The reaction mixture was then refluxed 4 1/2 h and on cooling it was diluted with light petroleum. The separated salts were filtered off and washed with boiling light petroleum. The filtrate and the washings were combined, concentrated and distilled. There was obtained a fraction boiling at 90–142°C/0.1 Torr 46.75 g (65.5% diphenyldimethoxysilane, 6.2% triphenylmethosilane and 31.8% *p*-chlorophenylmethoxysilane) and a fraction boiling at 180–220°C/0.1 Torr, 3.70 g. The bulk of the latter fraction was *p*-bis(diphenylmethoxysilyl)benzene, which was purified by crystallization from a benzene-methanol mixture; yield 3.32 g (6.0%), m.p. 149–151°C. For C₃₂H₃₀O₂Si₂ (502.7) calculated: 76.45% C, 6.01% H, 11.17% Si; found: 76.78% C, 5.98% H, 11.21% Si. NMR spectra: in the region of aromatic compounds was a doubled signal corresponding to 24 protons between $\delta = 6.903$ and 7.718. At $\delta = 3.504$ was a signal of 6 protons of the methoxy groups. The integral agreed with the structure proposed.

Reaction of p-dichlorobenzene with diphenyldimethoxysilane in xylene. The procedure being the same as that described above, 50 ml of tetrahydrofuran and 120 ml of xylene were employed. Sixty ml was distilled off in 30 min, then the reaction mixture was refluxed for 3 1/2 h. After cooling the inorganic salts were precipitated by the addition of light petroleum, collected on a filter and washed with benzene. The filtrate and the washings were combined and the solvents were removed by distillation. The crude product was crystallized from methanol; yield 36.55 g (66.0%) of *p*-bis(diphenylmethoxysilyl)benzene, m.p. 146–148°C. The product (10 g) was hydrolysed 10 min in 35 ml of boiling acetic acid containing 5 drops of 85% phosphoric acid. After the addition of 8 ml of boiling water and cooling the reaction mixture there was obtained the crude *p*-bis(diphenylhydroxysilyl)benzene (9.3 g), which was recrystallized from toluene, m.p. 222 to 229°C, undepressed with an authentic sample.

Reaction of p-dichlorobenzene with diphenyldiethoxysilane. This was carried out with magnesium powder or shavings, tetrahydrofuran, toluene or xylene being employed as solvent. The procedure and the ratio of the components were the same as in the reaction of *p*-dichlorobenzene with diphenyldimethoxysilane. The composition of the mixture after the reaction in toluene was determined quantitatively by gas chromatography. In the use of the magnesium shavings the liquid portion after crystallization of the product contained 38% of the unreacted diphenyldiethoxysilane, 4.7% of triphenylethoxysilane and 60% of *p*-chlorophenyldiphenylethoxysilane. With

magnesium in the powder form the respective portions of these compounds were 14, 4.5 and 37% (based on the starting mixture).

Reaction of p-dichlorobenzene with diphenylethoxychlorosilane in xylene. Powdered magnesium (10.7 g, 0.44 mol) was activated with a solution of *p*-dibromobenzene (2.37 g, 0.01 mol) and 3 drops of bromine in 50 ml of tetrahydrofuran. The mixture was refluxed 30 min, then a solution of diphenylethoxychlorosilane (57.75 g, 0.22 mol) and *p*-dichlorobenzene (14.70 g) in 120 ml of xylene was added in the course of 5 min. Sixty ml was distilled off during 1 h. After refluxing for the next 5 h the mixture was cooled and light petroleum was added. The salts were collected on a filter and washed with benzene. The filtrate and the washings were combined and the solvents were removed *in vacuo*. The residue was crystallized from absolute ethanol; yield 51.2 g (88.0%) of *p*-bis-(diphenylethoxysilyl)benzene, m.p. 157—158.5°C. The mixed melting point with a sample melting at 163—164°C was undepressed. The latter preparation was obtained by the reaction of diphenyldiethoxysilane with *p*-dibromobenzene and magnesium¹⁴. The filtrate left from the crystallized product was concentrated and distilled. There were obtained diphenyldiethoxysilane (formed from the unreacted diphenylethoxychlorosilane), *p*-chlorophenyldiphenylethoxysilane and a small amount of the product.

Reaction of p-dichlorobenzene with diphenylethoxychlorosilane in xylene and hydrolysis of the product. A flask was charged with *p*-dibromobenzene (0.1 mol), powdered magnesium (4.4 mol), 400 mol of tetrahydrofuran and 1 ml of an 80% benzene solution of the hydride. After 5 minutes' activation a solution of *p*-dichlorobenzene (1 mol) and diphenylethoxychlorosilane (2.2 mol) in 1200 ml of xylene with 1 ml of the hydride solution was added in the course of 70 min. Distillation of the mixture for 1 h removed 545 g of the solvent. The remaining mixture was then refluxed for 250 min. After cooling and the addition of 1200 ml of light petroleum the separated salts were filtered off and washed with 610 ml of xylene. The filtrate and the washings were combined and distilled under reduced pressure. The residue was boiled with 1000 g of glacial acetic acid and 8 g of 85% phosphoric acid for 15 min, then 200 ml of boiling water was added. Crystals of the product began to separate in a few minutes. The mixture was left standing at 5°C for 3 days, after which time the product was collected on a filter and thoroughly washed with water; yield of the crude *p*-bis(diphenylhydroxysilyl)benzene was 441.7 g (93%), m.p. 208—210°C.

Reaction of p-dichlorobenzene with diphenylmethoxysilane. The procedure was as in the case of the ethoxy derivative. *p*-Bis(diphenylmethoxysilyl)benzene, m.p. 149—151°C, was obtained in a yield of 80%.

REFERENCES

1. I.C.I.: French Pat. 1 469 801.
2. I.C.I.: French Pat. 1 557 712; Chem. Abstr. 71, 82085 (1969).
3. Normant H.: Compt. Rend. 239, 1510 (1954).
4. Metal and Thermit Corp.: Brit. Pat. 776 993 (1957); Chem. Abstr. 51, 17993 (1957).
5. Leebrick J. R., Ramsden H. E.: J. Org. Chem. 23, 953 (1958).
6. Ramsden H. E., Balint A. E., Whitford W. R., Walburn J. J., Cserr R.: J. Org. Chem. 22, 1202 (1957).
7. Ramsden H. E.: Brit. Pat. 824175; Chem. Abstr. 54, 8861 (1960).
8. Ramsden H. E., Balint A. E., Banks C. K.: Brit. Pat. 826 620 (1960); Chem. Abstr. 2570 (1961).
9. Omietanski G. M.: US-Pat. 3 053 872 (1962); Chem. Abstr. 58, 3457 g (1963).
10. Ballard D., Brennan T., Fearon F. W. G., Shiina K., Haiduc I., Gilman H.: Pure Appl. Chem. 19, 449 (1969).

11. Breed L. W., Haggerty jr W. J., Baiocchi F.: *J. Org. Chem.* **25**, 1633 (1960).
12. Cook H. A.: *Brit. Pat.* 671 553 (1952); *Chem. Abstr.* **47**, 4909 (1953).
13. Gilman H., Dunn G. E.: *J. Am. Chem. Soc.* **73**, 3404 (1951).
14. Bažant V., Černý M.: *This Journal* **39**, 1735 (1974).
15. Breed L. W., Elliott R. L.: *J. Organometal. Chem.* **9**, 188 (1967).
16. Beck H. N., Chaffee R. G.: *J. Chem. Eng. Data* **8**, 602 (1963).

Translated by J. Salák.