Arylene Silicon Compounds

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The *in situ* Grignard reaction between arylene halides and diorganomonochlorosilanes has yielded arylene silicon compounds, $HR_bR_cSiZSiR_cR_bH$, in which R_b and R_c are methyl and phenyl and Z is *p*-phenylene, *α,α′-p*-xylylene, 4,4′-diphenylene, 4,4′-diphenyleneoxy, bis-4,4′-(methylenephenylene)oxy, durylene, and 1,4-naphthylene. Careful hydrolysis of the bis-silanes yielded the corresponding silarylene diols.

WE WISH to report the preparation of new arylene silicon compounds by the *in situ* Grignard technique (*1-6*), Equation (1).

$$2\,HR_bR_cSiCl + BrZBr + 2\,Mg \xrightarrow{THF} HR_bR_cSiZSiR_cR_bH + MgBrCl \quad (1)$$

Table I lists the bis-silanes prepared and their physical properties, compounds I–XII. Compounds V and VIII were not isolated in pure state and remained after stripping to the indicated temperatures and pressures. Compounds VII and VIII were prepared from 4,4′-bis(chloromethylphenyl)ether; all others from the corresponding dibromo compounds. A reaction employing dimethylchlorosilane and 9,10-dibromoanthracene yielded a very complex mixture. Distillation gave a poor yield of an impure, viscous, yellow-green fluorescent liquid, b.p. 245 to 285° C. at 0.9 mm. of Hg, whose infrared spectrum was consistent with 9,10-bis(dimethylsilyl)anthracene. Calculated for $Si_2C_{18}H_{22}$: % C, 73.4; % H, 7.5 Found: % C, 74.8; % H, 8.4.

In many cases the corresponding silarylene diols, $HOR_bR_cSiZSiR_cR_bOH$, were isolated by carefully hydrolyzing the bis-silanes according to the procedure of Merker and Scott (*4*), Table I, compounds XIII–XXI. Compound XV was prepared from crude V, but the other diols were from purified silanes. Melting point determinations were initiated at room temperature. Condensation to siloxane most likely occurred during prolonged heating and contributed to the melting point ranges in some cases. Silanol analyses by the Grignard method were consistently low, possibly due to base-catalyzed condensation to siloxane and water. However, theoretical water was obtained from the polymerization of each diol to high polymer in benzene using tetramethylguanidine 2-ethylhexoate catalyst (*4*). The infrared spectra were consistent with the proposed structures and showed the compounds to be free of siloxane except for a trace in XVII and XXI. The attempted preparation of *p*-bis(phenylmethylhydroxysilyl)benzene from *p*-bis(phenylmethylsilyl)benzene, II, always gave polysiloxane instead of diol.

Preparation of Bis-silanes (I–XII). A solution of the dihalide (1 mole) in a minimum amount of tetrahydrofuran was added to a stirred mixture of magnesium turnings (2.5 gram-atoms), diorganochlorosilane (2.25 moles), and tetrahydrofuran (250ml.) at a rate sufficient to maintain gentle reflux. Extremely insoluble dihalides such as 4,4′-dibromobiphenyl and 1,4-dibromodurene were added slowly as slurries in tetrahydrofuran. Upon completion of addition the mixture was stirred and heated at gently reflux overnight. The mixture was then cooled and filtered. The residue was extracted by slurrying with *n*-hexane and filtered. The combined filtrate and extracts were washed free of magnesium salts with water and dried over sodium sulfate. After removal of solvent, the crude product was purified either by recrystallization or by reduced pressure distillation through a six-inch unpacked column.

Preparation of Diols (XIII–XXI). The bis-silane (1 mole) was added dropwise during a fifteen minute to one hour period to refluxing ethanol containing a small piece of sodium metal. Upon completion of addition the mixture was maintained at gentle reflux for several hours until hydrogen evolution ceased. The cooled mixture was added slowly to a stirred solution of sodium hydroxide (5 moles) in 700ml. methanol and 80ml. water. A solution of sodium hydroxide (5 moles) in 780ml. water was added to this solution during a period of 10 to 20 minutes. The resultant solution was allowed to stand one hour at room temperature. The sodium salt was hydrolyzed by dropwise addition of this solution during a 1½ to 2 hour period to a rapidly stirred solution of potassium diacid phosphate (7.6 moles) in excess ice water. The use of phosphoric acid instead of KH_2PO_4 gave nearly identical yields of diol; ammonium carbonate failed to give consistently good yields. The crude white diol was filtered, dried, and recrystallized from either benzene or *n*-hexane.

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Table I. Arylene Silicon Compounds, $R_aR_bR_cSiZSiR_cR_bR_a$

No.	R_a	R_b	R_c	Z	%, Yield[a]	Boiling Point[b]		n_D^{25}	d^{25}	R_D		%, Si	
						° C.	Mm. of Hg			Found	Calcd.[c]	Found[d]	Calcd.
I	H	[e]	[e]	—p-C_6H_4—	53	178	22	1.5445	0.9974	0.3232	0.3318	21.8	21.9
II	H	Ph	Me	—p-C_6H_4—	46.5	188	1.4	1.5892	1.027	0.3282	0.3296	17.5	17.6
III	H	Ph	Ph	—p-C_6H_4—	47	107–108[f,g]	...	...	...	...	...	12.6	12.7
IV	H	Me	Me	—4,4′-$C_6H_4C_6H_4$—	36	140–141	0.85	1.5742	0.9663	0.3413	0.3354	20.3	20.8
V	H	Ph	Ph	—4,4′-$C_6H_4C_6H_4$—	~80	[h]	...	...	...	...	...	10.6	10.8
VI	H	Me	Me	—4,4′-$C_6H_4OC_6H_4$—	68	135[i]	0.45	1.5478	0.976	0.3255	0.3181	19.5	19.6
VII	H	Me	Me	—4,4′-$CH_2C_6H_4OC_6H_4CH_2$—	93	155	0.6	1.5429	0.971	0.3245	0.3186	17.9	17.9
VIII	H	Ph	Ph	—4,4′-$CH_2C_6H_4OC_6H_4CH_2$—	41	[j]	...	...	...	...	...	9.78	9.98
IX	H	Me	Me	—4,4′-$CH_2C_6H_4CH_2$—	49	81[k]	0.8	1.5002	0.8703	0.3381	0.3340	25.0	25.2
X	H	Me	Me	—1,4-$C_{10}H_6$—	74	110–112	0.45	1.5765	0.973	0.3403	0.3355	23.2	23.0
XI	H	Me	Me	—[2,3,5,6-$(CH_3)_4C_6$]—	43	106–109[f,l]	...	...	...	...	...	21.8	22.4
XII	H	Me	Me	—m-C_6H_4—	48	58–59	1.1	1.4974	0.8703	0.3365	0.3355	28.5[m]	28.9
XIII	HO	Ph	Ph	—p-C_6H_4—	73	226–228[f]	...	...	...	...	...	11.4	11.8
XIV	HO	Me	Me	—4,4′-$C_6H_4C_6H_4$—	77	176–180[f,n]	...	...	...	...	...	17.8	18.6
XV	HO	Ph	Ph	—4,4′-$C_6H_4C_6H_4$—	23	191–193[f]	...	...	...	...	...	10.3	10.2
XVI	HO	Me	Me	—4,4′-$C_6H_4OC_6H_4$—	74	96[f,o]	...	...	...	...	...	16.4	17.6
XVII	HO	Me	Me	—4,4′-$CH_2C_6H_4OC_6H_4CH_2$—	45	84–88[f]	...	...	...	...	...	16.3	16.2
XVIII	HO	Me	Me	—4,4′-$CH_2C_6H_4CH_2$—	44	121–122[f,p]	...	...	...	...	...	22.1	22.1
XVIX	HO	Me	Me	—1,4-$C_{10}H_6$—	29	183–188[f]	...	...	...	...	...	18.9	20.3
XX	HO	Me	Me	—[2,3,5,6-$(CH_3)_4C_6$]—	38	146–150[f]	...	...	...	...	...	18.7	19.9
XXI	HO	Me	Me	—m-C_6H_4—	67	81.5–83.0[f]	...	...	...	...	...	24.9[q]	24.8

[a] Bis-silane yield based on dihalide; yield of diol based on bis-silane. [b] Uncorrected. [c] Based on values of A. I. Vogel, *et al.*, *J. Chem. Soc.* **531** (1952); *J. Phys. Chem.* **58**, 174 (1954). [d] Analyses by Analytical Laboratories, Research Department, Dow Corning Corp. [e] p-$HPhMeSiC_6H_4SiMe_2H$ from equimolar amounts of HPhMeSiCl and HMe_2SiCl. [f] Melting point, uncorrected, on Fisher-Johns apparatus. [g] From acetone. [h] Green solid, distilled to maximum T_{head} 256° C. at 0.63 mm. of Hg and T_{pot} 294° C. [i] D.R. Weyenberg, unpublished data, b.p. 120° C. at 0.7 mm. of Hg, n_d^{25} 1.5478, 41%. [j] Brown gum, distilled to maximum T_{head} 250° C. at 1.5 mm. of Hg and T_{pot} 310° C. [k] R.L. Merker and M.J. Scott, unpublished data, b.p. 132° C. at 20 mm. of Hg, n_d^{25} 1.5012, d^{25} 0.878, 73%. [l] From chloroform. [m] % C, found 61.7, calcd. 61.8; % H, found 9.6, calcd. 9.3. [n] Reported (5), 170–180° with decomposition, 90%. [o] Reported (5), 85–96.5° with decomposition, 90%. [p] R.L. Merker and M.J. Scott, unpublished data, m.p. 118.5–119°, 65%. [q] % C, found 52.8, calcd. 53.0% H, found 8.1, calcd. 8.0.

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