SYNTHESIS OF 1,4-BIS-(DIORGANOVINYLSILYL)-BENZENES

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Abstract

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SYNTHESIS OF 1,4-BIS-(DIORGANOVINYLSILYL)-BENZENES

Continuing our investigations on the study of organosilicon compounds with a phenylene bridge between silicon atoms, in the present work we report the synthesis of a new type of *p*-disilyl-substituted benzene—symmetrical 1,4-bis-(diorganovinylsilyl)-benzenes, which are of interest as monomers for obtaining high-molecular-weight compounds with alternating silylphenylene and silicon-carbon units.

As is known from the literature, much attention is currently being devoted to the synthesis of compounds with arylene units between silicon atoms. *p*-Disilyl-substituted benzenes are proposed to be obtained by various methods (1–13), but pure individual representatives of such compounds are still obtained in satisfactory yields only by organometallic methods.

We carry out the synthesis of 1,4-bis-(diorganovinylsilyl)-benzenes by an organomagnesium method, similarly to the synthesis of 1,4-bis-(diorganosilyl)-benzenes (14), according to the principle of simultaneous substitution of both bromine atoms in *p*-dibromobenzene by diorganovinylsilyl groups:

$$\mathrm{Br}\langle \mathrm{C_6H_4}\rangle \mathrm{Br} + \mathrm{Mg} \xrightarrow{\mathrm{THF}} \mathrm{BrMg}\langle \mathrm{C_6H_4}\rangle \mathrm{MgBr} + \mathrm{BrMg}\langle \mathrm{C_6H_4}\rangle \mathrm{Br}$$

$$\downarrow +\mathrm{XRR'SiCH{=}CH_2}$$

$$\mathrm{CH_2{=}CHRR'Si}\langle \mathrm{C_6H_4}\rangle \mathrm{SiR'RCH{=}CH_2} + \mathrm{CH_2{=}CHRR'Si}\langle \mathrm{C_6H_4}\rangle \mathrm{Br},$$

where: 1. $\mathrm{R} = \mathrm{R'} = \mathrm{CH_3};\ \mathrm{C_2H_5};\ \mathrm{C_6H_5}$. 2. $\mathrm{R} = \mathrm{CH_3};\ \mathrm{R'} = \mathrm{C_6H_5}$.

The reactions were carried out in tetrahydrofuran at the molar ratio of the starting components

$$\mathrm{Br}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Br} : \mathrm{Mg} : \mathrm{XRR'SiCH{=}CH_2} = 1 :\sim 2.3 : 2.$$

1,4-Bis-(dimethylvinylsilyl)- and 1,4-bis(diethylvinylsilyl)-benzenes were obtained by the interaction of the Grignard reagent of *p*-dibromobenzene with ethoxydimethyl- and chlorodiethylvinylsilanes, respectively:

$$\mathrm{Br}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Br{+}Mg} \xrightarrow{+\mathrm{OC_2H_5(CH_3)_2SiCH{=}CH_2}} \mathrm{CH_2{=}CH(CH_3)_2Si}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Si(CH_3)_2CH{=}CH_2}; \quad 21.0\%$$

$$\mathrm{Br}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Br{+}Mg} \xrightarrow{+\mathrm{Cl(C_2H_5)_2SiCH{=}CH_2}} \mathrm{CH_2{=}CH(C_2H_5)_2Si}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Si(C_2H_5)_2CH{=}CH_2}. \quad 26.8\%$$

1,4-Bis-(diorganovinylsilyl)-benzenes in which the organic substituents at the silicon atoms are aryl radicals were obtained in higher yields than in the case where the framing radicals are alkyl substituents. Monosilyl-substituted benzenes were also isolated (Table 1):

$$\mathrm{Br}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Br} + \mathrm{Mg} \xrightarrow{+\mathrm{ClR(C_6H_5)SiCH{=}CH_2}}$$

$$\to \mathrm{CH_2{=}CHR(C_6H_5)Si}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Si(C_6H_5)RCH{=}CH_2{+}Br}\left\langle \mathrm{C_6H_4} \right\rangle \mathrm{Si(C_6H_5)RCH{=}CH_2{+}MgBrCl},$$

where: 1. $R = CH_3$; yields of the mono- and disilyl derivatives were 3.5 and 43.5%, respectively. 2. $R = C_6H_5$; 2.7 and 44.6%.

Some physicochemical properties of the obtained mono- and *n*-disilyl derivatives of benzene with a vinyl radical at the silicon atom are given in Table 1.

Table 1

Physicochemical properties of mono- and *n*-disilyl-substituted benzenes

Compound	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Molecular weight found	Molecular weight calculated
$CH_2{=}CH(CH_3)_2Si{-}C_6H_4{-}Si(CH_3)_2CH{=}CH_2$	95/1	0.9123	1.5120	81.08	81.85	243244	246.4
$CH_2{=}CH(C_2H_5)_2Si{-}C_6H_4{-}Si(C_2H_5)_2CH{=}CH_2$	136-137/1	0.9268	1.5218	99.54	99.89	301300	303.3

Compound	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	MR_D found	MR_D calculated	Molecular weight found	Molecular weight calculated
$[CH_2{=}CH(CH_3)(C_6H_5)Si]_2{-}C_6H_4$	191–192/8 · 10^{-2}M.p. 33	1.0246	1.5892	121.91	121.49	367371	370.6
$CH_2{=}CH(C_6H_5)_2Si{-}C_6H_4{-}Si(C_6H_5)_2CH{=}CH_2$	M.p. 157–158	—	—	—	—	504507	494.7
$Br{-}C_6H_4{-}Si(CH_3)(C_6H_5)_2CH{=}CH_2$	143–144/1	1.2387	1.5917	81.99	81.61	299305	303.3
$Br{-}C_6H_4{-}Si(C_6H_5)_2CH{=}CH_2$	203–208/1M.p. 60–61	—	—	—	—	360361	365.3

The obtained 1,4-bis-(diorganovinylsilyl)-benzenes were used by us in addition reactions with mono- and dihydride silicon derivatives. Using 1,4-bis-(methylphenylvinylsilyl)-benzene as an example, it was shown ([15]) that 1,4-bis-(diorganovinylsilyl)-benzenes readily add hydride derivatives of silicon at both double bonds, with formation of compounds containing phenylene-carbon units:

$$CH_2{=}CH{-}Si(CH_3)(C_2H_5){-}C_6H_4{-}Si(CH_3)(C_6H_5){-}CH{=}CH_2$$
$$+\ 2(CH_3)_2C_6H_5SiH \xrightarrow{H_2PtCl_6}$$
$$\longrightarrow C_6H_5(CH_3)_2Si(CH_2)_2Si(CH_3)(C_2H_5){-}C_6H_4{-}Si(CH_3)(C_6H_5)(CH_2)_2Si(CH_3)_2C_6H_5.$$

With dihydride derivatives of silicon, for example with $CH_3C_6H_5SiH_2$, the obtained n-disilyl-substituted benzenes react according to the scheme of addition polymerization of two-component systems and give high-molecular-weight products with alternating silylphenylene and silicon-carbon units in the main chain.

Experimental Part

1) 1,4-Bis-(dimethylvinylsilyl)-benzene. To 17.0 g (0.7 g-atom) of magnesium in 350 ml of absolute tetrahydrofuran, 70.7 g (0.3 mole) of 1,4-dibromobenzene, dissolved in 120 ml of tetrahydrofuran, was added with stirring at such a rate that the temperature of the reaction mixture was 40–45°. After addition of the entire solution of 1,4-dibromobenzene, the flask with the reaction mixture was kept for 3 hr in a water bath, the temperature of which was within 7-10°. To the resulting crystalline Grignard reagent, 79.6 g (0.61

mole) of dimethylethoxyvinylsilane was slowly added, and then the mixture was heated at the boiling temperature for 2 hr, after which the tetrahydrofuran was distilled off and heating was again carried out for···

for 2 h at 90–93°. The magnesium salt was filtered off on a Büchner funnel and the filtrate was distilled.

15.5 g (yield 21.0%) of 1,4-bis-(dimethylvinylsilyl)-benzene was obtained. B.p. 95°/1 mm; d_4^{20} 0.9123; n_D^{20} 1.5120. MR_D found 81.08; calculated 81.85. Molecular weight: found 243; 244; calculated 246.4. Bromine number: found 129.6; 129.8; calculated 129.7.

Found, %:	C	68.10, 68.09;	H	8.49, 8.49;	Si	22.85, 22.71
$C_{14}H_{22}Si_2$. Calculated, %:	C	68.23;	H	8.99	Si	22.78

2) **1,4-Bis-(diethylvinylsilyl)-benzene.** To the organomagnesium compound prepared from 20 g (0.83 g-at.) of magnesium in 300 ml of absolute tetrahydrofuran and 78 g (0.33 mole) of 1,4-dibromobenzene in 120 ml of solvent, and crystallized over 6 h at room temperature, 98 g (0.66 mole) of diethylvinylchlorosilane was added over 3 h. The reaction mixture was heated for 1 h at the boiling temperature of tetrahydrofuran and then for another 2 h after 250 ml of tetrahydrofuran had been distilled off. The reaction products were isolated by a method analogous to that used for 1,4-bis-(dimethylvinylsilyl)-benzene.

15.5 g (yield 21.0%) of 1,4-bis-(diethylvinylsilyl)-benzene was obtained. B.p. 136–137°/1 mm; d_4^{20} 0.9268; n_D^{20} 1.5218. MR_D found 99.54; calculated 99.89. Molecular weight: found 300; 301; calculated 303.3. Bromine number: found 105.9; 106.1; calculated 105.6.

Found, %:	C	71.51, 71.60;	H	10.10, 9.99;	Si	18.54, 18.80
$C_{18}H_{30}Si_2$. Calculated, %:	C	71.44	H	9.99	Si	18.57

On distillation, a fraction was also isolated in an amount of 10.3 g (8.2%) with b.p. 73–76°/3 mm, corresponding to phenyldiethylvinylsilane: d_4^{20} 0.9074; n_D^{20} 1.5112. Molecular weight: found 188; 189; calculated 190.3. Bromine number: found 85.0; 85.2; calculated 84.2.

The chromatogram (Fig. 1), recorded at a temperature of ~ 250°, shows that the fraction contains ~ 90% phenyldiethylvinylsilane.*

3) The synthesis of 1,4-bis-(methylphenylvinylsilyl)-benzene was reported by us in [15].

4) **1,5-Bis-(diphenylvinylsilyl)-benzene.** The experiment was carried out analogously to the preparation of 1,4-bis-(diethylvinylsilyl)-benzene. To the organomagnesium compound prepared from 17 g (0.7 g-at.) of

Fig. 1. Chromatogram of the fraction 73-76°/3 mm

Figure 1: Fig. 1. Chromatogram of the fraction 73-76°/3 mm

magnesium in 300 ml of absolute tetrahydrofuran, 162 g (0.66 mole) of diphenylvinylchlorosilane was added. The reaction mixture was heated at 64-65° for 2 h.

After separation of the magnesium salt by filtration on a Büchner funnel and removal of tetrahydrofuran from the filtrate by distillation, a fraction up to 240°/1 mm was collected; from it, by redistillation, 1-bromo-4-diphenylvinylsilylbenzene was isolated in an amount of 6.5 g (yield 2.7%). B.p. 203-208°/1 mm; m.p. 60-61°**. Molecular weight: found 361; 360; calculated 365.3.

Found, %:	C	66.00, 65.97;	H	4.99, 5.00;	Si	7.75, 7.52
$C_{20}H_{17}SiBr$. Calculated, %:	C	65.75;	H	4.68	Si	7.69

Fig. 1. Chromatogram of the fraction 73-76°/3 mm

* The chromatogram was recorded on an LKhM-5 instrument (SKB IOC AS USSR): column with $l = 2$ m, $d_{\text{external}} = 6$ mm, stationary phase—PFMS-4, support—Inza brick, carrier gas—helium, supplied at a rate of ~ 60 ml/min.
** Without recrystallization.

The solid residue with b.p. above 240°/1 mm was recrystallized three times from benzene. A total of 73 g (yield 44.6%)* of 1,4-bis-(diphenylvinylsilyl)-benzene was obtained. M.p. 157-158°. Molecular weight: found 504; 507; calculated 494.7. Bromine number: found 54.00; 64.20; calculated 64.60.

$C_{34}H_{30}Si_2$.	Found, %:	C 81.91, 82.01;	H 6.11, 6.02;	Si 11.44, 11.38
	Calculated, %:	C 82.55,	H 6.12	Si 11.33

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* After the first recrystallization.

Note: Figure translations are in progress. See original paper for figures.

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