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

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Abstract

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CHEMISTRY

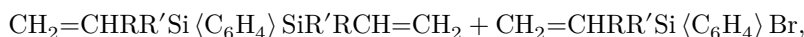
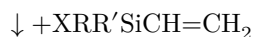
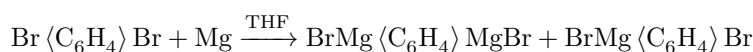
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SYNTHESIS OF 1,4-BIS-(DIORGANOVINYLSILYL)-BENZENES

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:

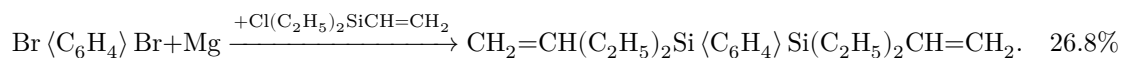
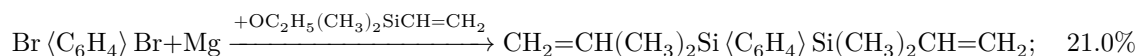


where: 1. R = R' = CH₃; C₂H₅; C₆H₅. 2. R = CH₃; R' = C₆H₅.

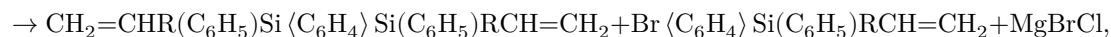
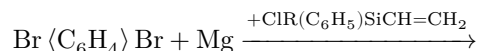
The reactions were carried out in tetrahydrofuran at the molar ratio of the starting components



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:



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):



where: 1. $R = \text{CH}_3$; yields of the mono- and disilyl derivatives were 3.5 and 43.5%, respectively. 2. $R = \text{C}_6\text{H}_5$; 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.

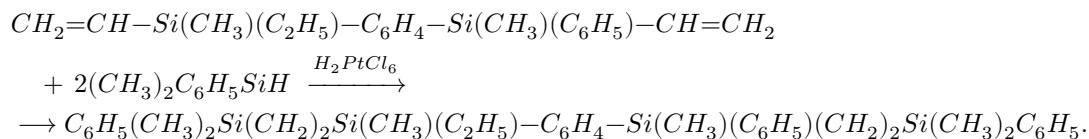
Table 1

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	
						weight found	weight calculated
$\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)_2\text{Si} \langle \text{C}_6\text{H}_4 \rangle \text{Si}(\text{C}_6\text{H}_5)_2\text{CH}=\text{CH}_2$	137/1	0.9268	1.5120	81.85	81.85	243244	246.4
$\text{CH}_2=\text{CH}(\text{C}_6\text{H}_5)_2\text{Si} \langle \text{C}_6\text{H}_4 \rangle \text{Si}(\text{C}_2\text{H}_5)_2\text{CH}=\text{CH}_2$	137/1	0.9268	1.5120	99.89	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
$[CH_2=CH(C_6H_5)(C_6H_5)]_2-C_6H_4$	192/8 · 10 ⁻² M.p.			121.91	121.49	367371	370.6
$CH_2=CH(C_6H_5)_2Si-C_6H_4-Si(C_6H_5)_2CH=CH_2$	33 157- 158				-	504507	494.7
$Br-C_6H_4-Si(CH_3)(C_6H_5)_2CH=CH_2$	144/1			81.99	81.61	299305	303.3
$Br-C_6H_4-Si(C_6H_5)_2CH=CH_2$	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:



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.

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