SYNTHESIS OF 3,4-BENZO-1-CHLORO-1-METHYL-1-SILACYCLOHEXANE AND SOME OF ITS DERIVATIVES

K. A. Andrianov, A. A. Zhdanov,
I. V. Karpova, and V. A. Odinets

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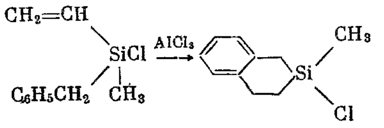
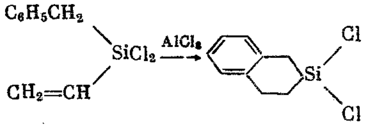
The addition of aromatic derivatives to vinylchlorosilanes has been studied with the interaction of vinylchlorosilanes with the formula $CH_2=CHR_nSiCl_{3-n}$ (with $R=CH_3$; $n=0, 1, 2, 3$) with benzene, toluene, chlorobenzene, and cumene as examples [1-3]. An intramolecular cyclization of vinylbenzyldichlorosilane and vinylbenzyldimethylsilane has also been carried out [4-5] in the presence of aluminum chloride.

In this work we investigated the intramolecular cyclization of vinylbenzylmethylchlorosilane. In the presence of aluminum chloride vinylbenzylmethylchlorosilane undergoes a change and forms a product with a somewhat higher boiling point, but possessing the same elemental composition. The formation of such a compound can be represented by the scheme

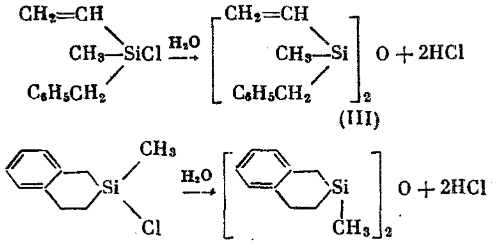

(I) (II)

The yield of (II) reaches 30-32%, whereas the yield of 3,4-benzo-(1,1-dichloro-1-silacyclohexane in the cyclization of vinylbenzyldichlorosilane according to the equation



reaches 44%. The data obtained agree with the data that we obtained in an investigation of the reactivity of the vinyl group of vinylchlorosilanes ($CH_2=CHR_nSiCl_{3-n}$, where $R=CH_3$, $n=0-3$) in the reaction of addition to benzene under the action of aluminum chloride [3].

To characterize the properties and structure of the synthesized compound, we produced certain derivatives (I) and (II). Hydrolysis of (I) and (II) yielded the corresponding disiloxanes (III) and (IV) according to the scheme


(III)

The IR spectra cited in Fig. 1 were taken for the synthesized disiloxanes. In a comparison of the spectra of these compounds, it can be seen that the absorption band in the region of 1610 cm^{-1}, characteristic

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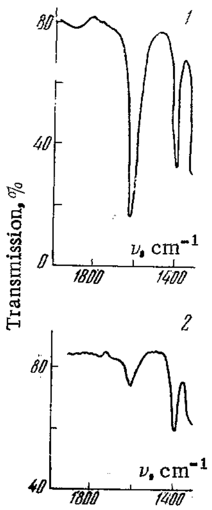
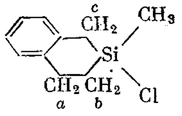


Fig. 1. IR spectra: 1) product of hydrolysis of vinylmethylbenzylchlorosilane; 2) product of hydrolysis of 3,4-benzo-1-chloro-1-methyl-1-silacyclohexane.

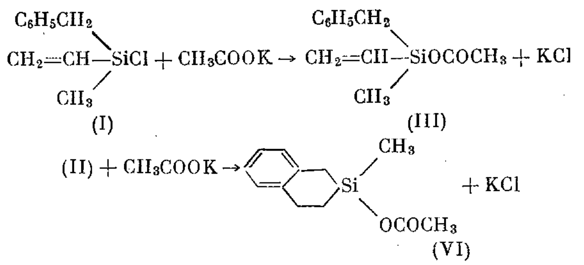
of the valence vibrations of the double bond in the vinyl group and observed in the spectrum of divinyldibenzyldimethyldisiloxane, is practically absent in the spectrum of the derivative. The low-intensity band observed in the spectrum of (II) at 1610 cm^{-1} is apparently due to vibrations in the bonds of the aromatic ring.

An analysis of the NMR spectra taken on a Hitachi H-60 spectrometer shows that in the spectrum taken for compound (II), the values of the chemical shifts of the hydrogen atoms of the methyl group comprise 0.3 ppm; for the methylene bridge $\overset{c}{\mathrm{CH_2}}$ this value is 2.20 ppm, for the CH_2 groups in the ethyl bridge these values are equal to 1.12 ppm for $-\overset{b}{\mathrm{CH_2}}-$ and 2.70 ppm for $-\overset{a}{\mathrm{CH_2}}-$. Chemical shifts of 7.00 ppm, corresponding to the hydrogens of the phenyl ring, are observed:



In the NMR spectra for compound (II), there are no shifts at all corresponding to the hydrogens of the vinyl group, the values of which lie in the region of 5.50-6.45 ppm. The total disappearance of the values of the shift for the hydrogens of the vinyl group and the presence of shifts characteristic of the methylene and ethylene groups, bound to the benzene ring and silicon atom, confirm the proposed structure of compound (II). A comparison of the IR spectra and an analysis of the NMR spectra permits us to consider that as a result of intramolecular cyclization of vinylbenzylmethylchlorosilane in the presence of aluminum chloride, 3,4-benzo-1-methyl-1-chloro-1-silacyclohexane is formed.

Acetoxy derivatives (V) and (VI) were produced by an exchange reaction of compounds (I) and (II) with potassium acetate, and then hydroxy-derivatives of vinylmethylbenzylchlorosilane and 3,4-benzo-1-methyl-1-chloro-1-silacyclohexane, (VII) and (VIII), were produced according to the schemes



The silanols of compounds (I) and (II) appear as oily liquids which condense upon standing, forming the corresponding disiloxanes. The composition and properties of the synthesized compounds are cited in Table 1.

EXPERIMENTAL

Vinylbenzylmethylchlorosilane. A Grignard reagent from 12 g of magnesium and 77 g benzyl chloride was added with cooling and vigorous mixing to 71 g vinylmethyldichlorosilane in 150 ml of ether. Then the reaction mixture was mixed for 4 h at 40°, cooled, and filtered. Ether was distilled off from the filtrate, and the residue redistilled under vacuum. Fractional distillation yielded 55 g (40%) of vinylbenzylmethylchlorosilane.

1-Chloro-1-methyl-3,4-benzo-1-silacyclohexane. Into a flask with a reflux condenser and mixer, containing 277 g vinylmethylbenzylchlorosilane, 12.74 g anhydrous $AlCl_3$ was introduced in small portions. The reaction mixture showed a strong temperature rise (to 150-160°) and darkened. Then the flask was heated for 4 h at 170°, cooled to 0°, and 8 g $(C_2H_5)_3N$ was added; after 30-40 min the liquid portion that separated was decanted, and it was fractionated under vacuum. Yield 95 g (35%) of 1-chloro-1-methyl 3,4-benzo-1-silacyclohexane.

TABLE 1. Composition and Properties of Synthesized Compounds

Compound No.	Yield, %	Bp., °C (p, mm Hg)	d_4^{20}	n_D^{20}	MR		Found, %				Empirical formula	Calculated, %			
					found	calculated	C	H	Si	Cl (OCOCH₃) (OH)		C	H	Si	Cl (OCOCH₃) (OH)
I	40	83—87(3)	1,0336	1,5215	58,40	58,37	61,15 60,85	6,64 6,52	13,86 14,00	18,39 18,38	$C_{10}H_{13}SiCl$	61,04	6,66	14,28	18,02
II	35	98—100(4)	1,0897	1,5330	56,13	56,71	60,45 60,42	6,57 6,69	14,34 14,13	18,18 18,32	$C_{10}H_{13}SiCl$	61,04	6,66	14,28	18,02
III	70	167—170(3)	0,9976	1,5310	105,02	105,93	69,75 70,03	7,56 7,67	16,44 16,49	—	$[C_{20}H_{26}Si]_2O$	70,94	7,74	16,59	—
IV	61	197—200(5)	1,0504	1,5510	102,82	102,91	70,08 69,88	7,59 7,69	16,87 17,04	—	$[C_{20}H_{26}Si]_2O$	70,94	7,74	16,59	—
V	51	97—100(4)	1,0161	0,5049	66,54	66,57	65,95 66,06	7,28 7,45	12,04 11,98	25,97 25,87	$C_{12}H_{16}SiO_2$	65,44	7,27	12,75	26,79
VI	52	96—102(1)	1,0612	1,5230	64,38	64,91	65,41 65,51	7,31 7,24	12,23 12,11	25,77 26,07	$C_{12}H_{16}SiO_2$	65,44	7,27	12,75	26,79
VII	73	—	0,9940	1,5285	55,46	56,70	68,00 68,19	7,85 7,93	16,36 16,01	8,96 8,87	$C_{10}H_{14}SiO$	67,35	7,91	15,75	9,54
VIII	51	—	1,0523	1,5505	53,91	54,47	67,15 67,40	7,76 7,82	15,23 15,45	9,45 9,47	$C_{10}H_{14}SiO$	67,35	7,91	15,75	9,54

Hydrolysis of Vinylbenzylmethylchlorosilane. In the reaction flask we placed 10 ml of water and 50 ml benzene, and 25 g vinylbenzylmethylchlorosilane in 25 ml benzene was introduced with mixing. Then the mixture was mixed for another 1.5 h at 40°, the organic layer removed, washed according to methyl orange, dried over Na_2SO_4, and the solvent distilled off. The residue was redistilled under vacuum. Fractional distillation yielded 15 g (70%) of the product.

Hydrolysis of 1-Chloro-1-methyl-3,4-benzo-1-silacyclohexane. From 50 ml of water, 50 ml of benzene, and 20 g of 1-chloro-1-methyl-3,4-benzo-1-silacyclohexane we obtained 10 g (61%) of the product.

Vinylbenzylmethylhydroxysilane. Vinylbenzylmethylacetoxysilane (5 g) was introduced into a mixture of 15 g of a 30% solution of Na_2SO_4, 15 ml of conc. NH_3, and 20 ml of ether, cooled with ice (2-5°). The ether layer was removed, washed with distilled water to a neutral pH according to bromothymol blue, and dried over Na_2SO_4. Then the ether was distilled off under vacuum. We obtained 2.78 g (73%) of the product.

Vinylbenzylmethylacetoxysilane. A mixture of 29 g anhydrous CH_3CO_2K, 70 ml toluene, and 45 g vinylbenzylmethylchlorosilane was heated with mixing for 6 h at 100° in a flask with a reflux condenser. After cooling and filtration, the solvent was distilled off from the filter, and the still residue was fractionated under vacuum. We obtained 29 g (52%) of vinylbenzylmethylacetoxysilane.

1-Acetoxy-1-methyl-3,4-benzo-1-silacyclohexane. Produced according to the procedure described from 92 g 1-chloro-1-methyl-3,4-benzo-1-silacyclohexane and 56 g potassium acetate in 100 ml of toluene; yield 53 g (51%).

3,4-Benzo-1-methyl-1-hydroxy-1-silacyclohexane. Produced from 45 g of a 30% solution of Na_2SO_3, 25 ml of ether, 15 ml of NH_3, and 12 g 3,4-benzo-1-methyl-1-acetoxy-1-silacyclohexane in a yield of 5.52 g (51%).

CONCLUSIONS

3,4-Benzo-1-chloro-1-methyl-1-silacyclohexane was synthesized by intramolecular cyclization of vinylbenzylmethylchlorosilane; its structure was demonstrated, and the properties of some of its derivatives were investigated.

LITERATURE CITED

1. G. H. Wagner, D. Z. Bailey, A. H. Pines, and M. Z. Dunhann, Industr. and Engng. Chem., 45, 368 (1953).
2. K. A. Andrianov, A. A. Zhdanov, and V. A. Odinets, Zh. Obshch. Khim., 31, 4033 (1961).
3. K. A. Andrianov, A. A. Zhdanov, and V. A. Odinets, Zh. Obshch. Khim., 32, 1126 (1962).
4. N. S. Nametkin, V. M. Vdovin, E. Sh. Finkel'shtein, and V. D. Oppenheim, Izv. Akad. Nauk SSSR, Otd. Khim. N., 45 (1964).
5. A. A. Zhdanov, K. A. Andrianov, V. A. Odinets, and I. V. Karpova, Zh. Obshch. Khim., 36, 521 (1966).