Reports of the Academy of Sciences of the USSR

Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN, V. M. VDOVIN,

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 154, No. 2

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR N. S. NAMETKIN, V. M. VDOVIN,
E. Sh. FINKELSHTEIN, T. N. ARKHIPOVA, V. D. OPPENGEIM

SYNTHESIS OF 3,4-BENZOSILICACYCLOPENTANES

The present work continues our investigations in the field of benzosilicacycloalkanes of the type

[[structural formula: benzene ring fused to a silacycloalkane ring with $(CH_2)_n$, CH_2, Si bearing two substit

Previously we succeeded in obtaining compounds of the indicated type, where $n = 2$, which are silicon-containing analogs of substituted tetralins (^{1}). In the present work we report the synthesis of a series of 3,4-benzosilicacyclopentanes ($n = 1$)—silicon-containing analogs of indane.

3,4-Benzo-1,1-dichlorosilicacyclopentane

[[structural formula: benzene ring fused to a five-membered ring $-CH_2 - SiCl_2 - CH_2-$]]

was mentioned in an American patent of 1953 as a product of the organomagnesium synthesis of *o*-dichlorosilylene and tetrachlorosilicon (^{2}). However, the patent gives neither reaction conditions, yields, nor any characteristics of the indicated preparation.

To obtain 3,4-benzo-1,1-dichlorosilicacyclopentane we used the reaction of silicon alkylation of aromatic compounds with chloroalkyl derivatives of silicon, previously employed only for obtaining open-chain arylalkylenesilanes (^{3,4}). Using chloromethylbenzyldichlorosilane as the cyclization substrate, we found that in benzene solution in the presence of aluminum chloride an intramolecular variant of this reaction can be successfully carried out (in 65–70% yield):

[[structural formula: o-ClCH$_2$C$_6$H$_4$CH$_2$SiCl$_2$]] $\xrightarrow[C_6H_6]{AlCl_3}$ [[structural formula: 3,4-benzo-1,1-dichlorosilicacyclop

According to the literature, chloromethylsilane chlorides are of low activity in the alkylation reaction of aromatic derivatives under Friedel–Crafts conditions (3,4). At the same time it is known that γ-chloroalkylsilane chlorides readily alkylate aromatic derivatives. However, our attempts to obtain 3,4-benzo-1,1-dichlorosilicacycloheptane ($n = 3$) from γ-chloropropylbenzyldichlorosilane $Cl(CH_2)_3Si(Cl_2)CH_2C_6H_5$ were unsuccessful.

3,4-Benzo-1,1-dichlorosilicacyclopentane was used to obtain 3,4-benzo-1,1-dihydrosilicacyclopentane, which is the complete silicon-containing analog of indane, as well as a series of substituted 3,4-benzosilica-

cyclopentanes according to the schemes:

$$\text{3,4-benzo-1,1-dichlorosilacyclopentane} \xrightarrow{\mathrm{LiAlH_4}} \text{3,4-benzo-1,1-dihydrosilacyclopentane}$$

$$\text{3,4-benzo-1,1-dichlorosilacyclopentane+RMgBr} \longrightarrow \text{3,4-benzo-1,1-dialkylsilacyclopentane}$$

where $R = \mathrm{CH_3};\ n\text{-}\mathrm{C_4H_9}$

$$\text{3,4-benzo-1,1-dichlorosilacyclopentane+}\mathrm{(CH_3CO)_2O} \longrightarrow \text{3,4-benzo-1,1-diacetoxysilacyclopentane}$$

To prove the structure of the compounds obtained by us, absorption spectra were recorded in the IR and UV regions.

The IR spectra of 3,4-benzosilacyclopentanes (Figs. 1, 2) contain a series of intense absorption bands characteristic of ortho-disubstituted

Fig. 1. IR spectrum of 3,4-benzo-1,1-dichlorosilacyclopentane

Fig. 2. IR spectrum of 3,4-benzo-1,1-dihydrosilacyclopentane

benzene rings. These are an intense double band in the region 750–730 $\mathrm{cm^{-1}}$, attributable to out-of-plane deformation vibrations of the C–H bonds of the benzene ring, and bands at 1150, 1075, and 1025 $\mathrm{cm^{-1}}$. In the region 2000–1650 $\mathrm{cm^{-1}}$, the group of absorption bands, with respect to the positions of the maxima and the relative intensities of the bands, is characteristic of an ortho-disubstituted benzene ring (5). The spectra of substituted 3,4-benzosilacyclopentanes in the region 1100–850 $\mathrm{cm^{-1}}$, which characterizes vibrations of the five-membered heterocycle, are analogous to the spectra of indanes (5).

Study of the UV spectra of 3,4-benzosilacyclopentanes gives additional confirmation of their structure. Thus, for example, the absorptions of 3,4-ben-

benzo-1,1-dihydrosilacyclopentane and indane (**6**) in the region 2400–3000 Å, having one and the same contour, only slightly shifted relative to one another (the bathochromic shift for 3,4-benzo-1,1-dihydrosilacyclopentane is ~30 Å) (Fig. 3).

Experimental Part

1. Starting substances: a) chloromethylbenzyldichlorosilane was obtained from 460 g (2.5 mol) of chloromethyltrichlorosilane, 126.5 g (1 mol) of benzyl chloride, and 36 g (1.5 mol) of magnesium by reverse addition of the Grignard reagent; b) γ-chloropropylbenzyldichlorosilane was obtained analogously from 212 g (1 mol) of γ-chloropropyltrichlorosilane, 63.2 g (0.5 mol) of benzyl chloride, and 24 g (1 mol) of magnesium.

2. Synthesis of 3,4-benzo-1,1-dichlorosilacyclopentane. In a three-necked flask equipped with an efficient stirrer, a reflux condenser, and a thermometer, 55 g (0.23 mol) of chloromethylbenzyldichlorosilane dissolved in 624 g (8 mol) of benzene was placed. With vigorous stirring, 26.6 g (0.2 mol) of aluminum chloride was added to the solution. The reaction was carried out at the boiling temperature of benzene until the evolution of hydrogen chloride ceased (4 h). After heating was completed, to bind the aluminum chloride, 30 g of calcined sodium chloride was added, the mixture was heated at 50° for one hour, and then the solid complex was filtered off. After distilling off the benzene, fractionation under vacuum gave 3,4-benzo-1,1-dichlorosilacyclopentane (see Table 1, No. 2).

3. Synthesis of 3,4-benzo-1,1-dihydrosilacyclopentane. In a three-

Table 1

No.	Yield, %	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Found, % Si	Found, % C	Found, % H	Found, % Cl (hydrolysis)	Calculated, % Si	Calculated, % C	Calculated, % H	Calculated, % Cl (hydrolysis)
1	53	90–92/3.5	1.5370	1.2680	59.01	59.01	–	–	–	30.10	–	–	–	29.59
2	73	82–84/4	1.5505	1.2517	52.74	52.74	20.96	71.70	7.55	35.20	20.92	71.57	7.54	34.91
3	66	190.5–192.5	1.5590	0.9865	43.94	44.04	17.39	73.91	8.61	–	17.30	73.99	8.71	–
4	83	209–211	1.5244	0.9417	52.77	52.78	11.37	78.17	10.67	–	11.40	77.97	10.63	–
5	64	159–160/5	1.5125	0.9159	80.81	80.40	11.25	57.54	5.78	–	11.22	57.57	5.64	–

Fig. 3. UV spectra of indane (1) and 3,4-benzo-1,1-dihydrosilacyclopentane (2)

Figure 1: Fig. 3. UV spectra of indane (1) and 3,4-benzo-1,1-dihydrosilacyclopentane (2)

No.	Yield, %	b.p., °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calculated	Found, % Si	Found, % C	Found, % H	Found, % Cl (hydrolysis)	Calculated, % Si	Calculated, % C	Calculated, % H	Calculated, % Cl (hydrolysis)
6	64	143–145/5	–	–	boiling point 38°	–	–	–	–	–	–	–	–	–
7	69	127–129/3.5	1.5350	1.2195	68.33	68.27	–	–	–	26.24	–	–	–	26.50

Notes: No. 1 –structural formula shown; No. 2 –structural formula shown with $SiCl_2$; No. 3 –structural formula shown with SiH_3; No. 4 –structural formula shown with $Si(CH_3)_2$; No. 5 –structural formula shown with $Si(CH_3)_3$; No. 6 –structural formula shown with $Si(OCOCH_3)_2$; No. 7 –structural formula shown with $Cl(CH_2)_3SiCl_2CH_2$ fused to the benzene ring.

A round-bottom flask equipped with a stirrer, reflux condenser, and dropping funnel was charged with 5.7 g (0.15 mole) of lithium aluminum hydride and 100 ml of absolute ether. To the stirred mixture, 20.3 g (0.1 mole) of 3,4-benzo-1,1-dichlorosilacyclopentane was added dropwise. The mixture was then heated for 3 hours. After completion of the experiment, the reaction mixture was hydrolyzed first with moist ether, and then with water. After separation of the ether layer and drying over calcium chloride, the products were distilled, as a result of which 3,4-benzo-1,1-dihydrosilacyclopentane was isolated (Table 1, No. 3).

Fig. 3. UV spectra of indane *(1)* and 3,4-benzo-1,1-dihydrosilacyclopentane *(2)*

4. Synthesis of 3,4-benzo-1,1-dimethylsilacyclopentane and 3,4-benzo-1,1-dibutylsilacyclopentane.

a) 3,4-Benzo-1,1-dimethylsilacyclopentane (Table 1, No. 4) was synthesized as a result of the reaction of 20.3 g (0.1 mole) of 3,4-benzo-1,1-dichlorosilacyclopentane with CH_3MgBr, obtained by bubbling methyl bromide through absolute ether in which 12 g (0.5 mole) of magnesium was stirred.

b) 3,4-Benzo-1,1-dibutylsilacyclopentane (Table 1, No. 5) was obtained by the organomagnesium method from 14 g (0.07 mole) of 3,4-benzo-1,1-

dichlorosilacyclopentane, 43.8 g (0.28 mole) of butyl bromide, and 12 g (0.5 mole) of magnesium.

5. Synthesis of 3,4-benzo-1,1-diacetoxysilacyclopentane.
In a two-necked flask equipped with a reflux condenser and thermometer were placed 5 g (0.024 mole) of 3,4-benzo-1,1-dichlorosilacyclopentane and 10 g (0.1 mole) of acetic anhydride. The mixture was heated to boiling (105°). After 15 min the temperature dropped to 82°, and boiling continued at this temperature for 3 hours. From the reaction products, acetyl chloride (50–52°) was first distilled off, and then, by distillation in vacuum, 3,4-benzo-1,1-diacetoxysilacyclopentane was isolated (Table 1, No. 6). IR spectra of 3,4-benzosilacyclopentanes were recorded on an IKS-14 spectrophotometer with a NaCl prism in the region 2000–650 cm^{-1} in a 0.006 mm layer.

UV spectra were recorded on an EPS-2 recording spectrophotometer in the region 2400–2900 Å at room temperature in a 0.5 cm cuvette. Solutions of the compounds were studied in spectrally pure isooctane at a concentration of 0.9–1.1 $\cdot 10^{-3}$ g-mole/l.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
28 IX 1963

CITED LITERATURE

1. V. M. Vdovin, N. S. Nametkin et al., *Izv. AN SSSR, ser. khim.*, 1964, No. 3.
2. I. M. Herch, U.S. Pat. No. 2615033 (1953); *Chem. Abstr.*, **47**, 9344 (1953).
3. E. A. Chernyshev, Doctoral dissertation, Moscow State University, 1962.
4. A. D. Petrov, V. F. Mironov et al., *Synthesis of Organosilicon Monomers*, Publishing House of the Academy of Sciences of the USSR, 1961, p. 340.
5. M. V. Shishkina, M. M. Kusakov, N. E. Tsytovich, *Izv. AN SSSR, ser. fiz.*, **26**, 1260 (1962).
6. M. M. Kusakov, E. A. Prokof' eva, M. V. Shishkina, *Optics and Spectroscopy*, **8**, 27 (1960).

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