Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. S. Nametkin, V. M. Vdovin,

1965

SovietRxiv

Abstract

Full Text

Chemistry

Corresponding Member of the Academy of Sciences of the USSR N. S. Nametkin,
V. M. Vdovin,
E. Sh. Finkelshtein, K. S. Konobeevskii, V. D. Oppengeim

Polymerization of 3,4-Benzo-1,1-dimethylsilacyclopentane

Previously we showed the possibility of obtaining polymers of the type

$$[-\mathrm{Si}-(\mathrm{CH}_2)_m-]_n \quad (m = 3, 4),$$

by catalytic cleavage of heterocycles,

$$(\mathrm{CH}_2)_m\mathrm{SiR}_2 \quad (m = 3, 4)$$

at the Si–C bond (1,2). In the present work we report the polymerization of the recently synthesized by us 3,4-benzo-1,1-dimethylsilacyclopentane

[structural formula of 3,4-benzo-1,1-dimethylsilacyclopentane] (3)

In the presence of 5-10 mole % aluminum chloride at temperatures of 50-100° for 8 hr, the indicated monomer was converted into a viscous oil of molecular weight up to 650 (cryoscopy in benzene) with a yield up to 65% (all experiments were carried out at atmospheric pressure in sealed ampoules placed in a thermostated shaker).

Polymerization of 3,4-benzo-1,1-dimethylsilacyclopentane to a solid polymer was carried out in the presence of metallic potassium as catalyst at temperatures of $\sim -100°$. The polymer was obtained in a yield up to 55%. It was a white powdery substance, melted at 158-160° (in a capillary), and dissolved in tetralin at $\sim 100°$.

To prove the structure of the polymers obtained, both oily and solid, IR spectra were recorded for products of different molecular weight (400, 600, and a high-molecular-weight product).

The spectra of the oil with molecular weight 400 (*b*) and of the solid polymer (*c*) are given in Fig. 1. In the same figure, for comparison, are given the spectra of the starting 3,4-benzo-1,1-dimethylsilacyclopentane (*a*) and of *o*-methyl-(trimethylsilylmethyl)benzene

Fig. 1. IR spectra: 3,4-benzo-1,1-dimethylsilacyclopentane (a); oily polymer with mol. wt. 400 (b); solid polymer (c); o-methyl-(trimethylsilyl)-benzene (d).

Figure 1: Fig. 1. IR spectra: 3,4-benzo-1,1-dimethylsilacyclopentane (a); oily polymer with mol. wt. 400 (b); solid polymer (c); o-methyl-(trimethylsilyl)-benzene (d).

[structural formula of *o*-methyl-(trimethylsilylmethyl)benzene] (*e*),

synthesized specially (4) as a model of the elementary unit of the polymer.

It is known from the literature (5) that ortho-substituted benzene derivatives have absorption bands in the regions 730–750, 1030, 1070, and 1150 cm^{-1}. All of them are present in the spectra of both 3,4-benzo-1,1-dimethylsilacyclopentane and the open-chain model. However, whereas in the spectrum of the former in the region 750 cm^{-1} there is an intense double band (730, 750 cm^{-1}), and the remaining bands have insignificant intensity, in the spectrum of the open-chain model the double band is replaced by a single one with a maximum at 740 cm^{-1}, and the intensity of the remaining three bands at 1030, 1070, and especially 1150 cm^{-1} increases sharply.

Comparing the spectra of the ring, the model, and the polymerization products, it may be noted that, on going from compounds with lower molecular weight to compounds with higher molecular weight, a successive increase is observed in the relative intensities of the bands at 1040 and 1150 cm^{-1}.

The absorption band at 1190 cm^{-1} behaves in an analogous manner; it is practically absent in the ring, has insignificant intensity in the sample with molecular weight 400, and increases on going to the spectrum of the solid polymer. In the model compound this band has rather high intensity.

Fig. 1. IR spectra: 3,4-benzo-1,1-dimethylsilacyclopentane (a); oily polymer with mol. wt. 400 (b); solid polymer (c); *o*-methyl-(trimethylsilyl)-benzene (d).

The intensities of the absorption bands at 1126 and 1208 cm^{-1} change in the reverse order. Both bands are very intense in the spectrum of 3,4-benzo-1,1-dimethylsilacyclopentane; on going to the spectrum of the oil with molecular weight 400 their intensity decreases, and it is still lower in the spectrum of the solid polymer. In the spectrum of the model, the band at 1126 cm^{-1} is completely absent, while that at 1208 cm^{-1} has insignificant intensity.

Finally, the absorption of the bands in the region 1550–1650 cm^{-1} changed. In work [6] it was pointed out that a characteristic feature of the spectra of 3,4-benzosilacyclopentanes is that the intensity of the 1575 cm^{-1} band is greater than that of the 1605 cm^{-1} band. In the open-chain model the intensity ratio is the reverse (the absorption bands at 1575 and 1605 cm^{-1} belong to the stretching

Fig. 4. X-ray diffraction pattern of the solid polymer of
3,4-benzo-1,1-dimethylsilacyclopentane

Figure 2: Fig. 4. X-ray diffraction pattern of the solid polymer of 3,4-benzo-1,1-dimethylsilacyclopentane

C=C vibrations of the benzene ring). The relative intensities of the absorption bands at 1575 and 1605 cm^{-1} in the spectra of the products

Fig. 4. X-ray diffraction pattern of the solid polymer of 3,4-benzo-1,1-dimethylsilacyclopentane.

polymerization have intermediate (between the ring and the model) values, and the ratio of intensities in the spectrum of the solid polymer approaches the value characteristic of the spectrum of the model.

All the changes discussed above in the spectra of the polymerization products can be explained if it is assumed that the polymerization of 3,4-benzo-1,1-dimethylsilacyclopentane proceeded with the formation of a polymer containing the grouping $|\,o\text{-}CH_2\text{—}C_6H_4\text{—}CH_2Si(CH_3)_2\text{—}\,|$ as the elementary unit. In the liquid polymerization products with low molecular weight (400; 600), unopened rings are present, possibly as end groups. The elemental analyses of the polymers are close to the elemental analysis of the monomer (Table 1).

Table 1

	Found, %	Found, %	Found, %	Calculated, %	Calculated, %	Calculated, %
	Si	C	H	Si	C	H
Solid product of low-temperature polymerization under the action of potassium	16.60	73.82	8.69	17.30	73.99	8.71

	Found, %	Found, %	Found, %	Calculated, %	Calculated, %	Calculated, %
Oil-like product, mol. wt. 600, of polymerization under the action of 5 mol. % aluminum chloride; 8 h at 80°	16.79	74.16	8.92	17.30	73.99	8.71

Thus, we consider it possible to represent the polymerization by the following scheme:

$$\text{3,4-benzo-1,1-dimethylsilacyclopentane} \longrightarrow [\,CH_2{-}o\text{-}C_6H_4{-}CH_2{-}Si(CH_3)_2\,]_n$$

It is known that, in the presence of metallic potassium in a solution of tetrahydrofuran (THF) or dimethoxyethane, alkyl- and silylalkyl-substituted benzenes are capable of forming ion-radicals through transfer of the electron of the valence shell of potassium to the benzene ring ([7]). On the other hand, it is known that ion-radicals are initiators of anionic polymerization ([8],[9]). We found that, on contact with a potassium mirror, a 20% solution of the monomer in THF at subzero temperatures, in particular at approximately −100° (the polymerization temperature), gives an electron paramagnetic resonance (EPR) spectrum consisting of a narrow singlet line 9 oersteds wide (Fig. 2b). In special experiments carried out by the method for obtaining ion-radicals ([10]), we succeeded in obtaining an EPR spectrum consisting of a quintet with a binomial distribution of intensities and a splitting between components of 4.3 oersteds (Fig. 2a). The presence of five lines can be explained by interaction of the unpaired electron with four protons of the *o*-disubstituted benzene ring. The width of the singlet

Fig. 2 and Fig. 3

Figure 3: Fig. 2 and Fig. 3

line (Fig. 2b) is equal to the splitting between the two middle components of the quintet (Fig. 2a).

These facts make it possible to suggest that ion-radicals are responsible for initiating the low-temperature polymerization described.

The polymerization of 3,4-benzo-1,1-dimethylsilacyclopentane was carried out by the following procedure. A 20% solution of the monomer in dry THF and a piece of potassium (for drying) were placed in side arm 1 of the special ampoule shown in Fig. 3. A piece of potassium was also placed in bulb 7. The ampoule was connected to a vacuum apparatus and evacuated to $5 \cdot 10^{-4}$ mm Hg.

Then a small amount of potassium was carefully distilled from bulb 7 onto the wall of arm 3, and bulb 7 was sealed off at constriction 4. The monomer solution was recondensed into arm 2, and arm 1 was sealed off at constriction 5. The ampoule was evacuated at 10^{-4} mm Hg for 2–3 h and sealed off at constriction 6. From arm 2 the solution was poured into arm 3, where a potassium mirror had been deposited. In the presence of the potassium mirror the solution acquired a yellow color; at temperatures of $+50$, $+20$, -30, and -65° (for 1 h) no visible signs of polymerization were observed. Only at temperatures close to the phase transition ($\sim -100^{\circ}$) did intense precipitation of a solid polymer occur; within a few minutes a solid block had already formed. After the polymer was washed on a filter with methanol and dried for 4 h at 80° in a vacuum oven, a white powdery polymer was obtained, the properties and composition of which were studied.

Fig. 2. ESR spectrum of the ion radical obtained from 3,4-benzo-1,1-dimethylsilacyclopentane by the method of [10], and the scale in oersteds (a). ESR spectrum obtained in the polymerization of 3,4-benzo-1,1-dimethylsilacyclopentane at 100° in THF solution over a potassium mirror, and the scale in oersteds (b).

Fig. 3. Ampoule for carrying out low-temperature polymerization.

The X-ray diffraction pattern of the solid polymer, shown in Fig. 4, indicates its crystalline structure.

The IR spectra of the compounds studied were obtained on a UR-10 spectrophotometer. Liquid products were recorded in a layer 0.005 cm thick, and the solid polymer as a KBr pellet (0.0015 g of polymer per 0.25 g of KBr). ESR spectra were recorded on an EPR-2 instrument.

The X-ray diffraction pattern of the polymer was recorded on a URS-60 X-ray unit (copper anticathode) by I. A. Litvinov.

Institute of Petrochemical Synthesis

named after A. V. Topchiev
Academy of Sciences of the USSR

Received
1 X 1964

CITED LITERATURE

1. V. M. Vdovin, N. S. Nametkin et al., *J. prakt. Chem.*, **281** (1964).
2. N. S. Nametkin, V. M. Vdovin, V. I. Zavyalov, *Izv. AN SSSR, OKhN*, 1964, No. 1.
3. N. S. Nametkin, V. M. Vdovin et al., *DAN*, **154**, No. 2, 383 (1964).
4. L. A. Leites, E. Sh. Finkel' shtein et al., *Izv. AN SSSR, Ser. Khim.*, 1965, No. 6.
5. M. V. Shishkina, M. M. Kussakov, I. E. Litovich, *Izv. AN SSSR, Ser. Fiz.*, **26**, 1260 (1962).
6. V. D. Olshevskii, E. Sh. Finkel' shtein, *Materials of the XV All-Union Conference on Spectroscopy*, Minsk, 1963.
7. S. P. Solodovnikov, E. A. Chernyshëv, *Zhurnal Strukturnoi Khimii*, **3**, No. 6, 665 (1962).
8. M. Szwarc, M. Levi, R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).
9. H. Brody, M. Ladacki et al., *J. Polym. Sci.*, **1**, 221 (1957).
10. V. V. Voevodskii, S. P. Solodovnikov, V. M. Chibrikin, *DAN*, **129**, 1082 (1959).

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