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Abstract

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CARBOFUNCTIONAL DERIVATIVES OF SILICACYCLOBUTANES

We have shown ([1–3]) that silicacyclobutanes are starting materials for obtaining high-molecular-weight heterochain silicon–hydrocarbon polymeric or telomeric products of the type $[R_3Si(CH_2)_3]_x$. However, up to the present time only silicacyclobutanes with R alkyl, aryl, or alkylaryl have been used in this reaction.

In order to expand the range of silicacyclobutane monomers, in the present work we synthesized a series of carbofunctional silicacyclobutanes (with a functional group in one of the radicals R), as well as a spiro silicon–hydrocarbon (see Table 1).

A silicacyclobutane with a cyanoalkyl radical was obtained by us by the reaction between methylhydridosilicacyclobutane and allyl cyanide in the presence of platinized charcoal.

In this reaction, the formation of condensation products of the silicacyclobutane derivative is appreciably less than in the case of the analogous reaction with ethylene ([4]), despite the higher reaction temperature. The latter could have been a consequence of the inhibiting effect of the nitrogen of the nitrile. In special experiments we established that the polymerization of silicacyclobutanes is inhibited not only by amines ([1]), but also by nitriles, while the telomerization of silicacyclobutanes with hydridosilanes ([3]) is inhibited by both the former and the latter.

Two other carbofunctional derivatives,

$$\begin{array}{c} —(CH_2)_3SiCH_3R \\ \quad\;\; | \quad\; | \end{array}$$

($R = —CH = CH_2$ and $—C_6H_4CH = CH_2$) were prepared from 1-chloro-1-methyl-1-silicacyclobutane and the corresponding Grignard reagents in diethyl ether.

These monomers are of special interest, since they contain vinyl–silicon and p-styryl groups, which are active in radical polymerization and copolymerization

processes. Thus, we have demonstrated the possibility of copolymerizing *p*-styrylmethylsilicacyclobutane with styrene and methyl methacrylate with the aid of azobisisobutyronitrile (AIBN). In both cases the reaction proceeded with participation of the multiple bond of the styryl derivative of silicacyclobutane, while the silicacyclobutane grouping entered the copolymer unchanged.

To obtain the spiro derivative, the reaction studied was:

$$(CH_2)_3SiCl_2 + M(CH_2)_4M \rightarrow (CH_2)_3Si(CH_2)_4 \qquad M = Li;\ MgBr.$$

When the dimagnesium derivative was used, the reaction led to the expected product in a yield of 49%. In the case where we used the dilithium derivative, which, as is known ([5]), gives better yields of 1,1-dimethylsilicacyclopentane (from dimethyldichlorosilane) than the dimagnesium derivative, in the reaction of dichlorosilicacyclobutane with 1,4-dilithiobutane only high-molecular-weight condensation products were formed. This observation, in our opinion, was the result of the specific properties of the silicacyclobutane grouping and prompted us to investigate the relation of the Si–C bond of the silicacyclobutane ring to the action of organometallic compounds. As such compounds we used–

magnesium bromobenzene and phenyllithium were used. It was found that the former compound practically does not react with 1,1-dimethyl-1-silacyclobutane in boiling ether, whereas phenyllithium cleaves the silacyclobutane grouping:

$$(CH_2)_3Si(CH_3)_2 \xrightarrow[\text{ether}]{LiC_6H_5} \xrightarrow{H_2O} n\text{-}C_3H_7(CH_3)_2SiC_6H_5$$
$$+ \text{ condensation products} \xleftarrow[\text{ether}]{C_6H_5MgBr} ClSi(CH_3)_2C_3H_7\text{-}n.$$

With a 3–5-fold excess of phenyllithium, the yield of *n*-propylphenyldimethylsilane reached 75%. The order of addition of phenyllithium to silacyclobutane was demonstrated by complete agreement of its properties, including IR spectra and gas–liquid chromatography data, with the properties of a preparation obtained by counter synthesis.

When an insufficient amount of phenyllithium is used, dimethylsilacyclobutane also enters completely into reaction, but in this case the main products are oily condensation products. According to elemental composition they proved to be silicon hydrocarbons; in the IR spectra frequencies of 1140, 1025, 990, 945, and 900 cm^{-1}, characterizing the grouping $\equiv SiCH_2CH_2CH_2Si \equiv$; 830, 875, and 1250 cm^{-1}–the grouping $\equiv Si–CH_3$, and a band at 2110 cm^{-1}, characterizing the $\equiv Si–H$ group, were observed; the presence of the latter was confirmed by the chemical method of Fritz–Burdt ([7]).

Experimental Part

1-Methyl-1-hydrido-1-silacyclobutane (I). To a solution of 5.7 g (0.15 mol) of lithium aluminum hydride in 100 ml of anhydrous ether, 37 g (0.3 mol) of 1-chloro-1-methyl-1-silacyclobutane ([6]) was added. The reaction was carried out in an argon atmosphere. The mixture was boiled for 3 h; the liquid products of the reaction mixture were condensed in vacuum and fractionated. 18.1 g of product I was obtained (see Table 1).

1-Cyanopropyl-1-methyl-1-silacyclobutane (II). 9.8 g (0.114 mol) of 1-methyl-1-hydrido-1-silacyclobutane and 30 g (0.45 mol) of allyl cyanide were heated for 13 h at 65° in the presence of 0.2 g of platinized charcoal (20% Pt). By distillation, 1.4 g of unreacted hydride and 3.95 g of product II were isolated.

1-Vinyl-1-methyl-1-silacyclobutane (III). To an ethereal solution of vinylmagnesium bromide, obtained from 110 g of vinyl bromide and 50 g of magnesium activated with iodine, 36 g of 1-chloro-1-methyl-1-silacyclobutane was added. After the usual work-up, 3.3 g of product III was isolated. When the reaction was carried out in THF, the yield of III according to gas–liquid chromatography was considerably higher; however, closely boiling by-products were formed.

1-*n*-Styryl-1-methyl-1-silacyclobutane (IV). To a solution of the Grignard reagent obtained from 14.6 g of *n*-chlorostyrene and 6 g of Mg in THF, 15 g of 1-chloro-1-methyl-1-silacyclobutane was added. After distillation in the presence of diphenylamine, 6 g of product IV was obtained.

Copolymerization of IV and styrene. 2 g of IV and 10 g of freshly distilled styrene in the presence of 0.015 g of AIBN were kept in a sealed ampoule for 8 h at $t = 80°$. The resulting reaction product was reprecipitated from a benzene solution with methanol. After drying to constant weight (95° at 15 mm), it was a white solid; molecular weight (cryoscopically in benzene) 1400, Si content 3.28% (determination of the sum of $\equiv Si(CH_2)_3$ and C=C groups) and rhodanine numbers (determination of C=C groups) established that the reaction product is a copolymer with a ratio of styryl and styrylsilacyclobutane units of $\sim 5 : 1$; the copolymer contains one terminal multiple bond. Evidence for the formation of the copolymer was obtained by heating the product at 180–200° for 2 h. As a result of opening of the silacyclobutane

Table 1

R — Si(CH$_3$) — CH$_2$CH$_2$CH$_2$ (ring)

R in monomer	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D* found	MR_D* calculated	Mol. wt. found	Mol. wt. calculated	Elemental and functional analysis found	Elemental and functional analysis calculated	IR absorption spectrum, cm^{-1}** characteristical frequencies for the ≡Si(CH$_2$)$_3$ grouping	IR absorption spectrum, cm^{-1}** other groups
H	70	65,5/760	1,4323	0,7773	28,78	28,91	86	86,2	Active hydrogen 1,17	1,16	1188, 1220	2120 — [≡Si—H]; 830, 865, 1255 — [≡Si—CH$_3$]
NCCH$_2$CH$_2$CH$_2$	25,8	102/10	1,4685	0,9104	47,05	46,80	157	153,3	Si — 18,37 C — 62,56 H — 9,86 N — 9,03	Si — 18,3 C — 62,67 H — 9,86 N — 9,13	1190, 1228	2249 —[—CN]; 830, 875, 1255 — [Si—CH$_3$]

R in monomer	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D* found	MR_D* calculated	Mol. wt. found	Mol. wt. calculated	Elemental and functional analysis found	Elemental and functional analysis calculated	IR absorption spectrum, cm^{-1}** characteristical frequencies for the $\equiv Si(CH_2)_{2-3}-$ grouping	IR absorption spectrum, cm^{-1}** other groups
$CH_2=CH-$	40—50	42/8	1,4520	0,8133	37,22	37,46	112,7	112,2	C — 64,26; H — 10,80; Rhodan number 99,6	C — 64,30; H — 10,78; Rhodan number 103,5	1185	1125, 955, 1010, 3050 — [≡ $Si—CH=CH_2$]; 830, 875, 1255 — [≡ $Si—CH_3$]
$CH_2=CH-C_6H_4-$	30—40	104—106/4	1,5596	0,9656	63,02	61,97	190	188,3	Si — 14,74; C — 76,46; H — 8,69; Rhodan number 63	Si — 14,91; C — 76,52; H — 8,57; Rhodan number 62	1185	1125, 990 — [≡ $C—CH=CH_2$]; 830, 875, 1255 — [≡ $Si—CH_3$]

R in monomer $\overset{R}{\underset{CH_3}{}}$ Si— CH_2 CH_2CH_2	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D* found	MR_D* calculated	Mol. wt. found	Mol. wt. calculated	Elemental and functional analysis found	Elemental and functional analysis calculated	IR absorption spectrum, cm^{-1}** characteristic frequencies for the $\equiv Si(CH_2)_3$— grouping	IR absorption spectrum, cm^{-1}** other groups
—$(CH_2)_3Si(CH_2)_4$—	49	62–63/30	1,4850	0,8959	40,06	40,41	126,3	126,25	Si—22,45 C—66,60 H—11,12	Si—22,23 C—66,59 H—11,19	1185 1025	1160, 1075, 1025, 860 — [$\equiv Si(CH_2)_4$—]

* With correction for the $\equiv Si(CH_2)_3$— group.

** The spectra were recorded by V. D. Odengeim on a UR-10 instrument in a thin layer.

groups, a completely crosslinked product is formed. The latter was extracted with benzene in a Soxhlet apparatus for 16 h—no loss of weight was observed. In a control experiment, a mixture of 2 g of the copolymer and 1 g of styrene homopolymer, obtained under the above conditions, was heated in an analogous manner.* After analogous extraction, 0.96 g of styrene homopolymer passed into the benzene solution.

Copolymerization of IV and methyl methacrylate. The copolymerization of IV and methyl methacrylate was carried out in an analogous manner. 5.44 g of methyl methacrylate and 1.14 g of IV, 0.076 g of AIBN, were used and heated at $t = 65°$ for 5 h. The reaction product was a colorless transparent solid

block. After reprecipitation with methanol from a benzene solution, the yield of copolymer was 65%, mol. wt. 3000. Found: Si 3.3%. By the bromine and rhodanine number method it was established that, in the copolymer molecule, for 24 methacrylate units there are 3 styrylsilicacyclobutane units. Heating the copolymer in a sealed ampoule at 180–200° for 5 h gives a 100% crosslinked product.

In all cases, frequencies characteristic of the silicacyclobutane ring were present in the IR spectra of the copolymers; in the spectra of the products subjected to heat treatment these frequencies were absent.

Tetramethylene, trimethylenesilane (V). To 95 g (0.75 mol) of 1,1-dichloro-1-silicacyclobutane in ether solution, with ice cooling, was added a Grignard reagent prepared from 216 g (1 mol) of dibromotetramethylenesilane and 73 g (3 mol) of magnesium. 35 g of product V was obtained.

Reaction of 1,1-dimethyl-1-silicacyclobutane with phenyllithium. To phenyllithium, prepared from 47.1 g (0.3 mol) of bromobenzene and 5.04 g (0.72 mol) of lithium in ether and filtered from unreacted lithium and lithium bromide, was added 5 g (0.05 mol) of dimethylsilicacyclobutane, and the mixture was heated for 5 h. All operations were carried out in an argon atmosphere. The reaction mixture was then decomposed with water. The ether extracts were dried. 6.3 g of a substance corresponding to phenyldimethylpropylsilane was isolated; b.p. 103°/29 mm; n_D^{20} 1.4950; d_4^{20} 0.8782; MR_D calculated 59.2; found 59.2.**

Found, %: C 74.4; Si 15.7; H 10.06
$C_{11}H_{18}Si$. Calculated, %: C 74.01; Si 15.8; H 10.17

To 9.6 g (0.096 mol) of dimethylsilicacyclobutane was added phenyllithium, prepared analogously to the preceding from 15.7 g (0.1 mol) of bromobenzene and 1.65 g (0.23 mol) of lithium. The reaction proceeded with appreciable evolution of heat. After 5 h of boiling, the reaction mixture was decomposed with water and then worked up in the usual manner. A small amount of substance with b.p. 103°/30 mm was isolated, which according to gas-liquid chromatography proved identical with propylphenyldimethylsilane, and ~ 7 g of oily products boiling from 100 to 280° at 7 mm. The fraction with b.p. 275–280°/7 mm has mol. wt. 709; 725. Found, %: C 63.93; Si 24.91; H 11.05; H_{act} 0.3; 0.26.

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* For better compatibility, both products were dissolved in benzene, after which the solution was evaporated to dryness under vacuum.

** Constants of phenyldimethylpropylsilane obtained from propyldimethylchlorosilane: b.p. 102-104°/30 mm Hg; n_D^{20} 1.4950; d_4^{20} 0.8801.

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