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

P. L. GRINBERG

1963

SovietRxiv

Abstract

Full Text

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

SILICACYCLOBUTANES

SYNTHESIS OF 1,1-SUBSTITUTED SILICACYCLOBUTANES

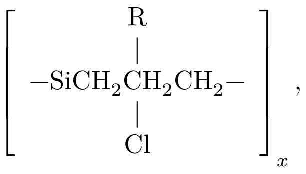
There is only a small amount of information in the literature concerning the synthesis and properties of silicacyclobutane compounds ([1]).

In the present work, the reaction (A) of organometallic ring closure of readily available ([2,3]) γ-chloropropyl derivatives of silicon was studied

$$\mathrm{Cl_2RSiCH_2CH_2CH_2Cl} \xrightarrow[\text{solvent}]{\text{M}} \mathrm{ClRSi(CH_2)_3} \tag{A}$$

$$\mathrm{R = CH_3;\ Cl;\ M = Na;\ Li;\ Mg}$$

Numerous experiments carried out with unactivated magnesium in ether led to low yields of silicacyclobutanes (usually less than 10%), and even these yields were difficult to reproduce. Changing the temperature and reaction time, using tetrahydrofuran and dibutyl ether as solvents, and sodium and lithium as the metals did not lead to positive results. In these cases either a polymer was formed–



$$\left[\begin{array}{c} \mathrm{R} \\ | \\ \mathrm{-SiCH_2CH_2CH_2-} \\ | \\ \mathrm{Cl} \end{array} \right]_x ,$$

or the starting γ-chlorides remained unchanged. Satisfactory (and well reproducible) yields,

Table 1

R	R^1	Method	Yield, %	B.p., °C/mm Hg	n_D^{20}	d_4^{20}	Found, % Si	Found, % C	Found, % H	Calculated, % Si	Calculated, % C	Calculated, % H
Cl	CH_3	A	65.0	103.5–104/atm	1.4482	0.9854	29.51; 29.60*			29.43	*	
Cl	Cl	A	30.3	114.5–114.8/atm	1.4620	1.1920	50.55; 50.67*			50.28	*	
CH_3	CH_3**	B	74.2	80.2–80.5/atm	1.4250	0.7700						
CH_3	C_2H_5***	B	68.4	65.5–66/160	1.4392	0.7920						
CH_3	C_2H_5	B	21.4	60–64/168	1.4408							
CH_3	*n*-C_4H_9	B	55.6	65.5–66/25	1.4455	0.8025	19.59; 19.22	67.17; 67.49	13.1; 13.29	19.7	67.5	12.8
CH_3	*n*-C_4H_9	B	19.1	42.5–46/18	1.4470			67.71; 67.84	13.25; 13.10		67.5	12.8
CH_3	phenyl	B	52.5	61.5–62/5	1.5349	0.9511	17.88; 17.6	73.51; 73.71	8.66; 8.80	17.25	74.0	8.64
CH_3	benzyl	B	87.3	73.5–74/5	1.5313	0.9400	16.11; 16.34	74.81; 74.60	9.13; 9.23	15.9	75.1	9.08
CH_3	allyl****	B	60.3	53/50	1.4571	0.8150		67.60; 67.84	11.43; 11.36		66.6	11.1

* Amount of hydrolyzable chlorine, %.
** Data (5) for 1,1-dimethylsilicacyclobutane obtained from $BrCH_2CH_2CH_2Si(CH_3)_2Cl$: b.p. 81°, n_D^{20} 1.4270, d_4^{20} 0.7746.
*** Data (4) for 1-methyl-1-ethylsilicacyclobutane: b.p. 109 (745 mm), n_D^{20} 1.4388; d_4^{20} 0.7965.
**** Molecular weight found by the cryoscopic method in benzene: 124.0, 125.0; calculated 126 for $C_7H_{14}Si$.

chlorine-substituted silacyclobutanes only when using magnesium activated with iodine vapor.

Earlier attempts[4,5] to cyclize γ-halopropylchlorosilanes with magnesium led to a high yield of the silacyclobutane derivative only when γ-bromopropyldimethylchlorosilane was used, which, however, is obtained by a complicated multistage synthesis[5].

We further established that the chlorine-substituted silacyclobutanes obtained by us can be successfully used for preparing silacyclobutanes with alkyl, aryl, alkenyl, and alkylaryl substituents at silicon. In the reaction

$$Cl(CH_3)Si(CH_2)_3 \xrightarrow[\text{ether}]{R'MgX} R'(CH_3)Si(CH_2)_3 \qquad (B)$$

$R' = CH_3$; C_2H_5; n-C_4H_9; $-CH_2CH{=}CH_2$; $-CH_2-C_6H_5$; $-C_6H_5$; X = Cl, Br, I

chloro-, bromo-, and iodo-derived organomagnesium compounds were successfully used.

Table 2

RR′Si$(CH_2)_3$	RR′Si$(CH_2)_3$	MR_D^*, found A	MR_D^*, calculated B	ΔMR_D (A–B)	MR_D, calculated with correction	Source
R	R′					
Cl	CH_3	32.80	32.41	+0.39	32.91	Present work
Cl	Cl	32.56	32.04	+0.52	32.54	Ibid.
CH_3	CH_3	33.21	32.78	+0.43	33.28	»
CH_3	C_2H_5	37.94	37.29	+0.65	37.79	»
CH_3	n-C_4H_9	47.13	46.59	+0.54	47.09	»
CH_3	phenyl	53.12	52.60	+0.52	53.10	»
CH_3	benzyl	58.00	57.41	+0.59	57.91	»
CH_3	allyl	42.11	41.75	+0.36	42.25	»
C_2H_5	Cl	37.45	36.92	+0.53	37.42	(4)
CH_3	Cl**	37.67	37.22	+0.45	37.72	(4)
RR′Si$(CH_2)_4$	RR′Si$(CH_2)_4$					
CH_3	CH_3	37.54	37.41	+0.13	–	(11)
n-C_3H_7	n-C_3H_7	55.98	55.93	+0.05	–	(11)
H	H	28.65	28.67	−0.02	–	(11)
H	CH_3	33.04	33.04	0.0	–	(12)
$ClCH_2$	CH_3	42.5	42.5	0.0	–	(13)
RR′Si$(CH_2)_5$	RR′Si$(CH_2)_5$					
CH_3	CH_3	41.92	42.04	−0.12	–	(11)
Cl	CH_3	41.57	41.67	−0.10	–	(13)
H	CH_3	37.67	37.67	0.00	–	(12)
n-C_3H_7	n-C_3H_7	60.56	60.56	−0.10	–	(14)
n-C_4H_9	n-C_4H_9	69.74	69.82	−0.08	–	(14)

---

[*] The calculation was carried out using the table of group refractions (^{10}).

[**] In the compound $(CH_3)ClSiCH_2CH(CH_3)CH_2$.

Noticeable cleavage of the Si—C bond in the silacyclobutane grouping under the reaction conditions was not observed*.

We also investigated the possibility of obtaining silacyclobutane hydrocarbons by the combined ring-closure—alkylation scheme

$$Cl_2(CH_3)SiCH_2CH_2CH_2Cl + 2Mg + R'X \rightarrow R'(CH_3)Si(CH_2)_3 \tag{B}$$

$$R'X = C_2H_5Br;\ n\text{-}C_4H_9Br;\ CH_3I$$

However, the corresponding silacyclobutanes were obtained in low yields and contained impurities that were difficult to separate.

The properties of 1,1-substituted silacyclobutanes and the yields of products obtained by reactions (A)—(B) are presented in Table 1.

In calculating MR_D for the compounds obtained, we noted the presence of stable exaltation. From the data presented in Table 2 it is evident that, both in our examples and in silacyclobutanes known from the literature, such exaltation is observed.

However, if the value of MR_D for the $Si-(CH_2)_3-$ group is taken not as 17.64 (according to Warrick (8)), but, with the correction calculated by us (+0.50), as 18.14, then quite satisfactory agreement is obtained between the calculated and found values of MR_D.

Such a considerable exaltation in MR_D in silicacyclobutanes apparently has the same nature as in other "strained" rings, in particular cyclopropanes (9). In this connection it is interesting to note that, in substituted silicacyclopentanes and silicacyclohexanes, a noticeable exaltation of MR_D is absent.

The MR_D values of several silicacyclopentane and silicacyclohexane compounds whose purity is reliable are given in Table 2. The starting γ-chlorides were synthesized by the method of addition of hydrosilanes to allyl chloride with an H_2PtCl_6 catalyst (3).

Synthesis of 1-chloro-1-methylsilicacyclobutane by method (A). To 144 g (6 mol) of magnesium in a two-necked vessel, isolated from atmospheric moisture, 10 g of crystalline iodine was sublimed. The magnesium thus activated, 1200 g (6.2 mol) of γ-chloropropylmethyldichlorosilane, and 800 ml of ether were heated on a water bath for ~ 40 h. Stirring (until the formation of a monolithic mass) was continued for ~ 30 h. During heating of the reaction mixture, an additional 2.5-3 l of ether was added. After filtration from the precipitate, triple washing of the precipitate with ether, and fractionation on a column, 470 g (3.9

---

[*] As is known from literature data (6,7), when magnesium iodoalkyls act on allylchlorosilanes ($(CH_2{=}CHCH_2)$

mol) of 1-chloro-1-methylsilicacyclobutane, b.p. 103.5–104°, and 200 g of the starting γ-chloride were isolated.

The yield of 1-chloro-1-methylsilicacyclobutane can be increased to 75% by using an excess of activated magnesium and adding it gradually to the reaction mixture.

Synthesis of 1-methyl-1-benzylsilicacyclobutane by method (B) was carried out from 40 g (1.7 mol) of magnesium, 140 g (1.11 mol) of benzyl chloride, and 54 g (0.448 mol) of 1-chloro-1-methylsilicacyclobutane in 500 ml of ether. The reaction mixture was heated for 4 h and decomposed with water. After the usual workup and vacuum distillation, 69 g (0.39 mol) of 1-benzyl-1-methylsilicacyclobutane was obtained, b.p. 73.5–74°/5 mm Hg.

Synthesis of 1-ethyl-1-methylsilicacyclobutane by method (B) was carried out from 191.5 g (1 mol) of γ-chloropropylmethyldichlorosilane, 55 g (2.3 mol) of magnesium, and 115 g (1.05 mol) of ethyl bromide by boiling the reaction mixture in 700 ml of ether. After decomposition of the reaction mixture with water, 24.5 g (0.21 mol) of 1-ethyl-1-methylsilicacyclobutane was isolated, b.p. 60–64°/168 mm, and 69.5 g (yield 41.5%) of sym-di-(γ-chloropropyl)-dimethyldiethyldisiloxane, b.p. 134–140°/5 mm.

Omission of the stage of decomposition of the reaction mixture with water does not lead to a substantial improvement in the yield of 1-ethyl-1-methylsilicacyclobutane.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

Received
12 II 1963

REFERENCES

1. C. Eaborn, *Organosilicon-Compounds*, London, 1960, p. 370.
2. J. L. Speir et al., *J. Am. Chem. Soc.*, **82**, 3601 (1960).
3. V. F. Mironov, V. V. Nepomnina, *Izv. AN SSSR, OKhN*, 1960, 2140.
4. A. D. Petrov, V. A. Ponomarenko et al., *Izv. AN SSSR, OKhN*, 1957, No. 10, 1216.
5. L. H. Sommer, L. A. Baum, *J. Am. Chem. Soc.*, **76**, 5002 (1954).
6. V. M. Vdovin, K. S. Pushchevaya, A. D. Petrov, *Izv. AN SSSR, OKhN*, 1961, 1275.

7. A. D. Petrov, G. I. Nikishin, *Izv. AN SSSR, OKhN*, 1956, 243.
8. E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).
9. S. S. Batsanov, *Usp. khim.*, **24**, No. 6, 688 (1955).
10. V. F. Mironov, G. I. Nikishin, *Izv. AN SSSR, OKhN*, No. 9, 1081 (1958).
11. A. F. Platé, N. A. Belikova, Yu. P. Egorov, *DAN*, **97**, No. 5, 847 (1954).
12. R. West, *J. Am. Chem. Soc.*, **76**, 6012 (1954).
13. V. M. Vdovin, N. S. Nametkin et al., *Izv. AN SSSR, OKhN*, 1963, No. 2.
14. H. Rosenberg, J. D. Groves, Chr. Tamborski, *J. Org. Chem.*, **25**, No. 2, 246 (1960).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.