UDC 547.128

REACTION OF DICHLOROSILANES WITH LITHIUM IN THE PRESENCE OF ARYLETHYLENES*

O. M. Nefedov, M. N. Manakov, V. N. Medvedev, A. S. Kachaturov, and V. I. Shiryaev

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 2, No. 2, pp. 299–310, 1966

The reaction of organodichlorosilanes ($RR'SiI_2$ and $RSiHCl_2$) and mono- or diarylethylenes with metallic lithium in tetrahydrofuran gives the corresponding substituted silacyclopentanes in 25–75% yield. The general character of the reaction is demonstrated and the optimal conditions are found. The suggested structure is completely confirmed by a study of certain physical and chemical properties of the aryl-substituted silacyclopentanes. IR and NMR spectra are presented. It has been demonstrated by gas-liquid chromatography and NMR spectroscopy that the x,x'-diaryl-1,1-dialkyl-silacyclopentanes formed from $RR'SiCl_2$, $ArCH{=}CH_2$ and lithium contain several possible isomers, which result from the position of the aryl substituents relative to one another or to the plane of the salicyclopentane ring.

We have previously shown [2] that it is possible to prepare aryl-substituted 1,1-dimethylsilacyclopentanes and polymers with the $-Si(CH_3)_2-$ grouping in the main chain by reacting dichlorodimethylsilane and styrene or its analogs with sodium or lithium in tetrahydrofuran (THF). The reaction was carried out by adding a mixture of $(CH_3)_2SiCl_2$ and styrene (1:2 mole ratio) to the alkali metal in the THF at 60–70° C (the boiling point of the reaction mixture). The yields of the substituted silacyclopentanes ranged from 25–50% depending on the structure of the initial arylethylene.

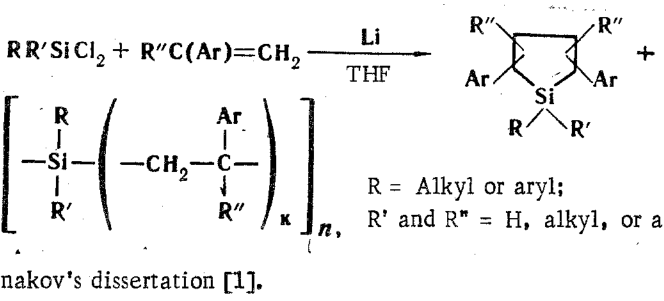
To find the optimal conditions we studied the reaction between $(CH_3)_2SiCl_2$ and styrene for the influence of temperature (-20 to 60° C) and silane: ethylene ratio (from 1:1.5 to 1:3) on the yield and proportions of the reaction products.

It is seen from the data of Table 1 that the maximum yield of x,x'-diphenyl-1,1-dimethyl-1-silacyclopentane (I, $R = CH_3$) was obtained with a stoichiometric ratio of the reactants, i.e., with $(CH_3)_2SiCl_2$: styrene = 1:2. If the ratio was changed in either direction, the relative amount of polymeric material increased, the yield of I ($R = CH_3$) dropped and it became more difficult to separate. The optimum temperature lay in the range from 0–30° and this was apparently also true when styrene was replaced by other monoarylethylenes, e.g., vinyltoluene, α-methylstyrene, etc. (see Table 1). Dilution of the THF with either diethyl ether or benzene to a ratio of 1:4–6 had no noticeable effect on the reaction (Table 1).

These optimal conditions for the formation of silacyclopentanes, found originally for dichlorodimethylsilane, were applied to other dichlorodiorganosilanes which had been shown previously to react with alkali metals and conjugated dienes in the same way as $(CH_3)_2SiCl_2$ [3]. It is seen from Table 1 that under these conditions the yields of the silacyclopentanes from monoarylethylenes were 25–75%, while those from diarylethylenes were 25–40%. It is also clear that aryl- and alkenyl-substituted dichlorosilanes can be used in place of the dialkyldichlorosilanes.

The reaction of styrene and lithium with dichlorosilane (H_2SiCl_2) and monoalkyldichlorosilanes (CH_3SiHCl_2, $C_2H_5SiHCl_2$) was of particular interest, since it could give silacyclopentanes containing the highly reactive Si–H bond. However, these compounds were obtained, in yields of not more than 20–25%, only in experiments with alkyldichlorosilanes carried out at temperatures of -50 to $-60°$. The products of H_2SiCl_2 (even at $-60°$) and $AlkSiHCl_2$ (above $-20°$) were polymeric silahydrocarbons, which in some cases contained no Si–H bonds (IR spectra) and probably had a network structure. This is probably because metallation occurred at Si–H as well as at Si–Cl in the highly polar THF (μ = 1.7 D) (see [4], for example).

Thus the reaction of organodichlorosilanes and arylethylenes with alkali metals can be expressed by the following general equation:



R = Alkyl or aryl;
R' and R" = H, alkyl, or aryl.

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* Part of M. N. Manakov's dissertation [1].

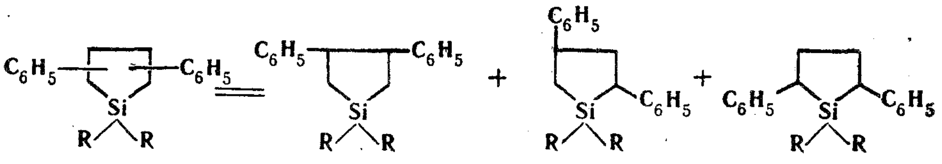
Table 1

Results of Reaction of $RR'SiCl_2$ and Arylethylenes with Lithium

Dichlorosilane, $RR'SiCl_2$	Arylethylene, (AE)	Mole ratio AE: $RR'SiCl_3$	Solvent	Temperature, ° C	Substituted 1-silacyclopentane produced	
					Substituents	Yield, %
$(CH_3)_2SiCl_2$	Styrene	2 : 1	THF	60	x, x'-Diphenyl-1, 1-dimethyl-	46
"	"	"	"	30	"	61
"	"	"	"	0	"	63
"	"	"	"	−20	"	60
"	"	1.5 : 1	"	0	"	50
"	"	2.5 : 1	"	0	"	56
"	"	3 : 1	"	0	"	36
"	"	2 : 1	THF-C_6H_6 (1 : 4)	50	"	47
"	"	"	THF-C_6H_6 (1 : 10)	60	"	36
"	Vinyltoluene	"	THF	60	x, x'-Ditolyl-1, 1-dimethyl	49
"	Vinylxylene	"	"	0		65
"	"	"	"	0	x, x'-Dixylyl-1, 1-dimethyl	53
"	Vinylmesitylene	"	"	0	x, x'-Dimesityl-1, 1-dimethyl	42
"	α-Methylstyrene	"	"	70	x, x'-Diphenyl-1, 1, X, X'-tetramethyl-	28
"	"	"	"	0		48
"	trans-Stilbene	1.5 : 1	"	60	2, 3, 4, 5-Tetraphenyl-1, 1-dimethyl-	35
"	1, 1-Diphenylethylene	2 : 1	"	35—40	x, x, x', x', -Tetraphenyl-1, 1-dimethyl-	23
$(C_2H_5)_2SiCl_2$	Styrene	"	"	30—35	x, x'-Diphenyl-1, 1-diethyl-	75
"	Vinyltoluene	"	"	0	x, x'-Ditolyl-1, 1-diethyl-	72
$C_6H_5Si(CH_3)Cl_2$	Styrene	"	"	0	1, x, x'-Triphenyl-1-methyl-	24
"	Vinyltoluene	"	"	0	x, x'-Ditolyl-1-phenyl-1-methyl-	25.5
$(CH_2{=}CHCH_2)_2SiCl_2$	Styrene	"	"	0	x, x'-Diphenyl-1, 1-diallyl-	27
$C_2H_5SiHCl_2$	"	"	"	From −60 to −65	x, x'-Diphenyl-1-ethyl-	20

The probable mechanism of this reaction has been discussed in detail elsewhere [2, 5]. It should be noted here that in most experiments the crude silacyclopentanes contained small amounts of the corresponding disilacyclohexanes [5] according to gas-liquid chromatographic (GLC) data.

As noted earlier, the silacyclopentanes formed from organodichlorosilanes, arylethylenes, and lithium are evidently mixtures of isomers with different positions of the aryl groups relative to each other and to the silacyclopentane nucleus. For example, the following isomers are possible from the reaction of R_2SiCl_2 with styrene:



I Ia Iб Iв

Moreover, cis-trans isomers are also possible for some of the compounds Ia-Ic. However, we were not able to separate any of the isomers of I (R = CH_3) completely by thin-layer chromatography on Al_2O_3 or by GLC on a variety of columns (200 × 0.4 cm 10% Apiezon M or 15% polyethylene glycol succinate on Chromosorb W, 2.5% silicone Siss on NaCl, 10% poly(vinylmethylsiloxane) on Celite; temperature 200–250° C; carrier gas, helium or argon). Only with GLC of 1,1-dimethyl-x,x'-diphenyl-1-silacyclopentane on a 200 × 0.4 cm column of 15% Apiezon L on Chromosorb W at 225° C (instrument made at the Institute of Organic Chemistry, AS USSR with helium as the carrier gas) or on 120 × 0.4 cm column of 0.5% polyethylene glycol adipate on Chromosorb W or 5% Wacker highly vinylated silicone on Celite 545 at 150–200° C (Pye flame-ionization chromatograph with argon carrier gas) was partial separation of the isomers achieved (two incompletely resolved peaks with an area ratio of ~ 50:50, see, for example, Fig. 1). Further attempts were made to determine the relative amounts of the isomers of I (R = CH_3)) from the NMR spectra, which contained three different signals for CH_3 groups bonded to silicon with τ 9.71, 10.13, and 10.60 and relative intensities of 26:52:22 (Fig. 2). That these lines were due to different isomers and not to spin-spin coupling was demonstrated by taking the NMR spectra at different frequencies (40 and 30 Mc). This phenomenon is evidently explained by the different effect of the phenyl groups in isomers Ia, Ib, and Ic or the cis- and trans- forms of one of these on the methyl groups, which causes different chemical shifts to appear for the methyl protons. If the three isomers Ia, Ib, and Ic are present in I (R = CH_3), their relative amounts are 26, 52, and 22%, while if the mixture contains the cis- and trans-isomers of only one of them, e.g., in agreement with the data for 2, 5-diphenyl-1,1-dimethyl-1-silacyclopentane (Ic), the relative proportions are 48:52%. It should be noted that the ratio of (22 + 26) : 52 is very close to the value of 50:50 found by GLC analysis.

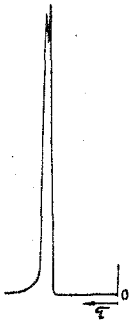


Fig. 1. Chromatogram of x, x'-dimethyl-1-silacyclopentane (I, R = = CH_3; mixture of isomers). Pye chromatograph with flame-ionization detector; 1.2 m of 0.5% of polyethylene glycol adipate on 60–80 mesh Chromosorb W; temperature 150° C; carrier gas, argon at 60 ml/min.

By analogy with the results obtained for I (R = CH_3), it may be postulated that the other substituted silacyclopentanes formed from organodichlorosilanes, arylethylenes, and lithium are also mixtures of isomers with varying positions of the aryl groups.

The structures of the substituted silacyclopentanes, which we prepared for the first time, were demonstrated by elemental analysis, molecular weight, and IR and NMR spectroscopy.

The IR spectra (Fig. 3) were recorded on a UR-10 double-beam spectrometer as thin films (liquid compounds, ~ 0.02 mm) or KBr pellets (solids). The benzene ring vibrations in the aryl-substituted silacyclopentanes occurred in the 1400–1600 cm^{-1} region, the silicon-methyl groups at 1240–1260 cm^{-1}, and the methylene groups at 2800–3100 cm^{-1}.

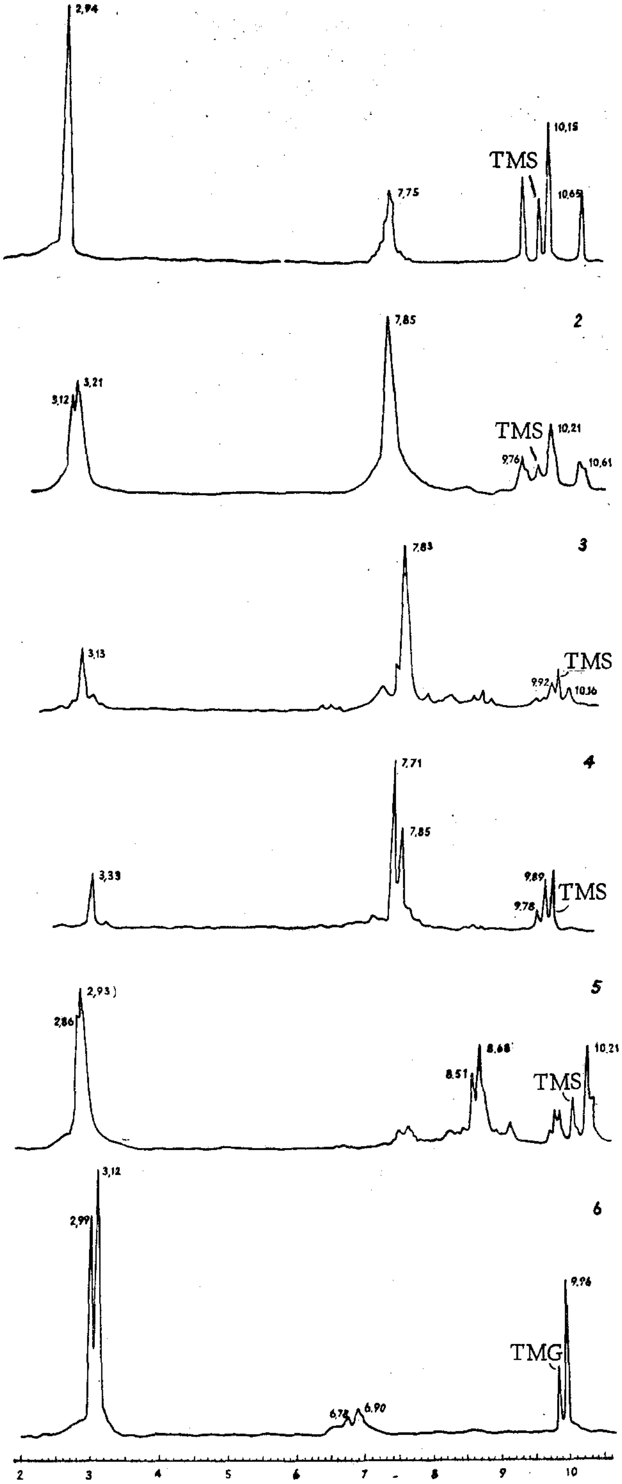


Fig. 2. NMR spectra of substituted silacyclopentanes. 1) x, x'-diphenyl-1, 1-dimethyl-1-silacyclopentane; 2) x, x'-ditolyl-1, 1-dimethyl-1-silacyclopentane; 3) x, x'-dixylyl-1, 1-dimethyl-1-silacyclopentane; 4) x, x'-dimesityl-1, 1-dimethyl-1-silacyclopentane; 5) x, x'-diphenyl-1, 1, x, x'-tetramethyl-1-silacyclopentane; 6) 2, 3, 4, 5-tetraphenyl-1, 1-dimethyl-1-silacyclopentane.

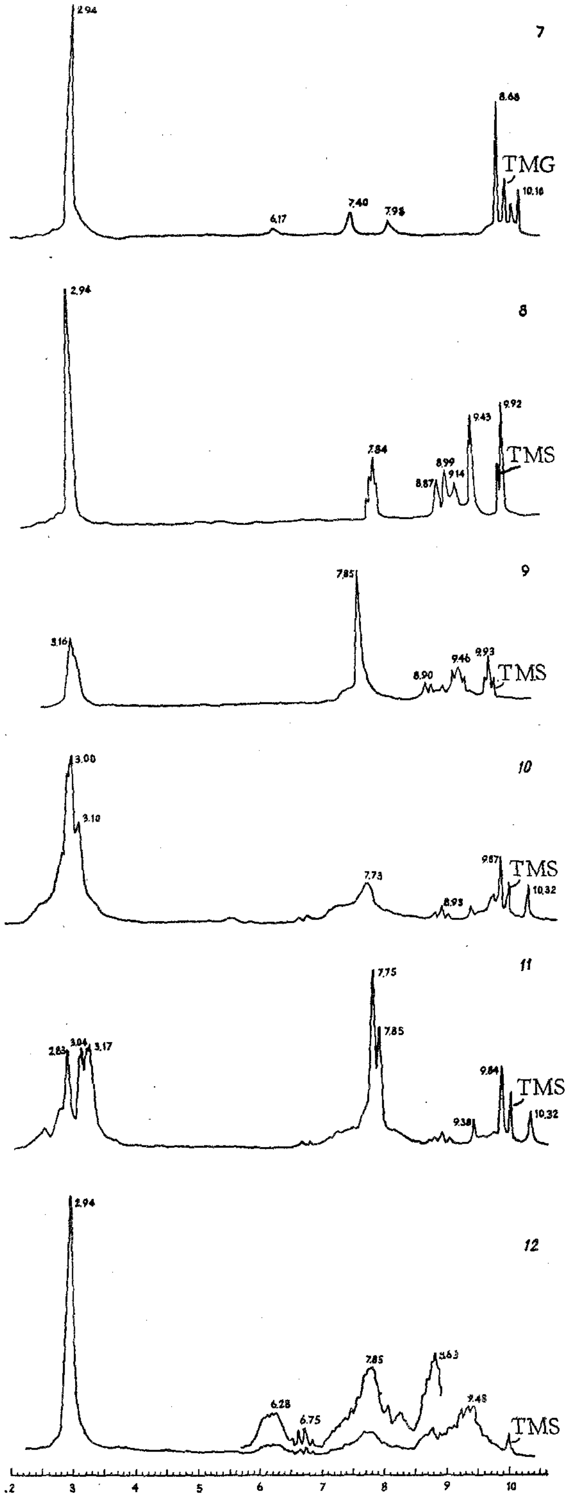


Fig. 2. (cont'd) 7) x, x, x', x'-tetraphenyl-1, 1-dimethyl-1-silacyclopentane; 8) x, x'-diphenyl-1, 1-diethyl-1-silacyclopentane; 9) x, x'-ditolyl-1, 1-diethyl-1-silacyclopentane; 10) 1, x, x'-triphenyl-1-methyl-1-silacyclopentane; 11) x, x'-ditolyl-1-phenyl-1-methyl-1-silacyclopentane; 12) x, x'-diphenyl-1-ethyl-1-silacyclopentane.

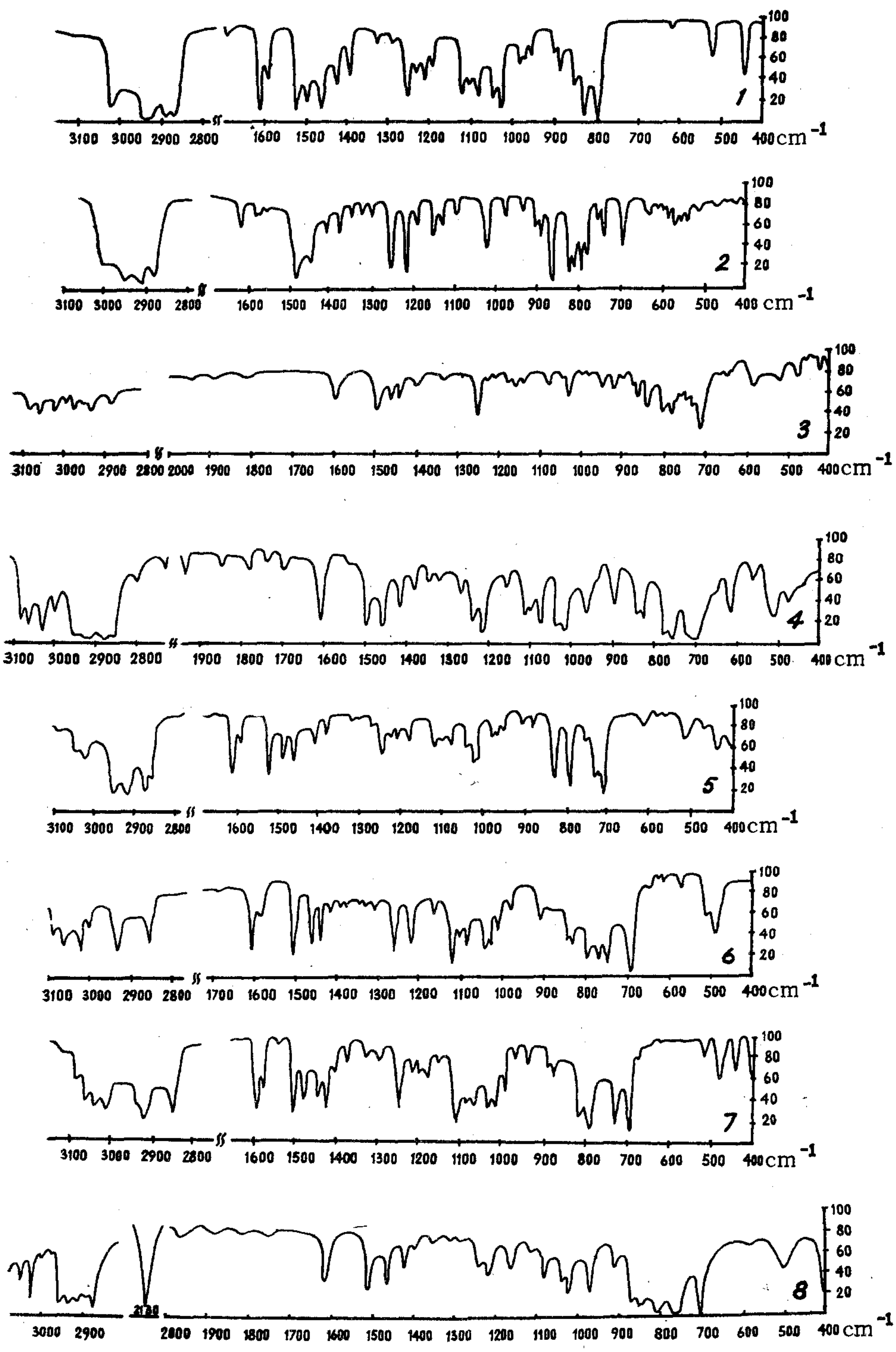


Fig. 3. IR spectra of substituted silacyclopentanes. 1) x, x'-dixylyl-1, 1-dimethyl-1-silacyclopentane; 2) x, x'-dimesityl-1, 1-dimethyl-1-silacyclopentane; 3) x, x, x', x'-tetraphenyl-1, 1-dimethyl-1-silacyclopentane; 4) x, x'-diphenyl-1, 1-diethyl-1-silacyclopentane; 5) x, x'-ditolyl-1, 1-diethyl-1-silacyclopentane; 6) 1, x, x'-triphenyl-1-methyl-1-silacyclopentane; 7) x, x'-ditolyl-1-phenyl-1-methyl-1-silacyclopentane; 8) x, x'-diphenyl-1-ethyl-1-silacyclopentane.

Table 2

Properties of Substituted 1-Silacyclopentanes

Substituent	Bp, ° C (pressure, mm)	d_4^{20}	n_D^{20}	Molecular formula	Found					Calculated				
					MR_D	M*	C, %	H, %	Si, %	MR**$_D$	M	C, %	H, %	Si, %
x, x'-Dixylyl-1, 1-dimethyl-	170—172 (0.8)	0.9812	1.5530	$C_{22}H_{30}Si$	105.1	313	81.79 81.75	9.21 9.40	8.52 8.69	104.3	322	81.92	9.38	8.70
x, x'-Dimesityl-1, 1-dimethyl-	205—207 (0.8)	mp. 87—88°	—	$C_{24}H_{34}Si$	—	340	82.03 82.11	9.85 9.63	7.87 7.79	—	350	82.22	9.78	8.00
x, x, x', x'-Tetraphenyl-1, 1-dimethyl-	236—238 (0.7)	mp. 180.5—181.5°	—	$C_{30}H_{30}Si$	—	412	86.55 86.85	7.55 7.64	6.17 6.31	—	418	86.05	7.17	6.78
x, x'-Ditolyl-1, 1-diethyl-	174—175 (1.0)	1.0186	1.5664	$C_{22}H_{30}Si$	103.3	306	81.44 81.63	9.11 9.23	8.48 8.65	104.3	322	81.92	9.38	8.70
1, x, x'-Triphenyl-1-methyl	183—185 (1.0)	1.0674	1.6010	$C_{23}H_{24}Si$	105.4	314	83.57 83.69	7.80 7.53	9.01 9.07	105.6	328	84.09	7.37	8.54
x, x'-Ditolyl-1-phenyl-1-methyl-	195—196 (1.0)	1.0550	1.5940	$C_{25}H_{28}Si$	114.7	339	83.76 83.91	7.80 7.68	7.48 7.62	114.9	356	84.25	7.86	7.89
x, x'-Diphenyl-1, 1-diallyl-	187—188 (0.6)	1.0125	1.5744	$C_{22}H_{26}Si$	103.8	309	82.80 83.00	7.94 8.09	8.46 8.64	103.4	318	82.96	8.23	8.81
x, x'-Diphenyl-1-ethyl-	156.5 (0.25)	1.0149	1.5773	$C_{18}H_{22}Si$	87.0	252	80.72 80.94	8.17 8.11	10.22 10.30	86.0	266	81.14	8.33	10.53

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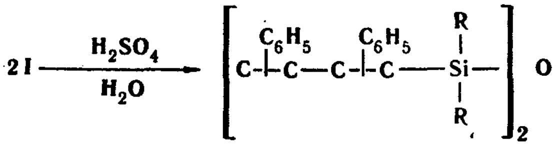
* Cryoscopic in benzene

** From bond refractivities [11].

The H^1 NMR spectra (Fig. 2) were recorded on high-resolution (10^{-8}) spectrometers of the JNM-3 or JNM-C-60 types at 40 or 60 Mc at room temperature as the pure substances or as saturated solutions in CCl_4. Tetramethylsilane (TMS, τ 9.87) were used as internal standards. In agreement with the literature [7, 8], the methyl and methylene groups attached to silicon had $\tau \sim 10$, and 8.5–9.5, respectively. The hydrogen nuclei of the benzene rings of the C-substituted di- and tetra-arylsilacyclopentanes gave signals with $\tau \sim 3$, which is also in agreement with the literature [8].

Certain chemical reactions also demonstrated that these were derivatives of silacyclopentane. In particular, the x, x'-diaryl-1,1-dialkyl-1-silacyclopentanes (e.g., I) were readily converted into the corresponding siloxanes (60–80% yields) by concentrated sulfuric acid:

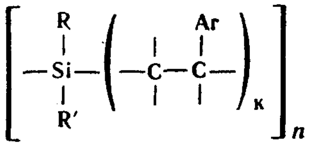


$$2\,I \xrightarrow[H_2O]{H_2SO_4} \left[C{-}\overset{C_6H_5}{C}{-}C{-}\overset{C_6H_5}{C}{-}C{-}\underset{R}{\overset{R}{Si}}{-} \right]_2 O$$

This is precisely analogous to the known ring-opening of 1, 1-dimethyl-1-silacyclopentane by sulfuric acid [9]. A similar scission of one of the Si–C bonds of the silacyclopentane ring occurred with bromine in methanol at ~ 20°, i.e., under the conditions for determination of the bromine number by the Kaufman technique (approximately 70% reaction in 3–4 hr).

Some of the properties and analysis data for the new substituted silacyclopentanes are presented in Table 2.

As noted earlier, high-molecular products with silicon atoms in the main chain are produced along with the silacyclopentanes. These materials are slightly colored viscous liquids (resins) or powders (after reprecipitation). The over-all structure of these polymers was indicated by elemental analysis and IR and H^1 NMR spectroscopy.



$$\left[-\underset{R'}{\overset{R}{Si}}- \left(-C-\overset{Ar}{C}- \right)_{\kappa} \right]_n$$

The linearity of the polymers formed from diorganodichlorosilanes and styrenes was confirmed by thermomechanical studies.

Experimental

1, 1-Diphenylethylene was prepared by the dehydration of diphenylmethanol (prepared from C_6H_5MgBr and butyl acetate) over anhydrous $CuSO_4$. It was purified by distillation. Bp 105.5–106° (2 mm), n_D^{20} 1.6079. According to [10], bp 277° (760 mm), n_D^{20} 1.6075. The purity of the initial arylethylenes and organodichlorosilanes, which were obtained by distillation of commercial products, was checked by chromatography [2].

All the experiments on the synthesis of substituted silacyclopentanes were carried out, as before [2], under pure dry nitrogen by adding a mixture of the organodichlorosilane and the arylethylene to finely dispersed lithium in THF with vigorous stirring, which was continued until tests for hydrolyzable chlorine were negative.

x, x'-Diphenyl-1, 1-dimethyl-1-silacyclopentane was prepared from $(CH_3)_2SiCl_2$, styrene, and lithium in THF in the yield quoted in Table 1. Properties additional to those recorded previously [2] were: bp 152–153° C (0.45 mm), n_D^{20} 1.5769; freezing point –34 to –35° C (glass); kinematic viscosity ν^{20} 35.8 cst, ν^{50} 7.4 cst, ν^{100} 2.0 cst. GLC data (Fig. 1) showed the presence of at least two isomers. The H^1 NMR spectrum showed signals (Fig. 2) at τ 2.94 (C_6H_5 group), 7.76 (CH_2 group), and 9.71, 10.13, and 10.60 (CH_3 groups of the various isomers). The 10:4:6 ratio of the intensities of the C_6H_5, CH_2, and CH_3 signals is close to the theoretical value.

The NMR spectra of the polymers formed in this experiment showed signals at $\tau \sim 10.0$ (CH_3 attached to Si), ~ 8.3 (CH_2), and ~ 3.0 (C_6H_5).

x, x'-Ditolyl-1, 1-dimethyl-1-silacyclopentane was prepared from $(CH_3)_2SiCl_2$, vinyltoluene, and lithium. Its IR spectrum may be found in [2], its properties in Table 1, and its NMR spectrum in Fig. 2.

x, x'-Dixylyl-1, 1-dimethyl-1-silacyclopentane. A mixture of 9.7 g (0.075 mole) dichlorodimethylsilane and 19.8 g (0.15 mole) of vinylxylene (mixture of isomers, n_D^{20} 1.5286) was added over 90 min at 0° C to a well-stirred suspension of 2.1 g (0.3 g atom) of finely dispersed lithium in THF. After normal work-up the reaction products were fractionated to give 12.8 g (53%) of dixylyldiemethylsilacyclopentane, the properties and spectroscopic curves of which are given in Table 2 and Figs. 2 and 3. The yield of polymers was 8 g.

x, x'-Diesityl-1, 1-dimethyl-1-silacyclopentane was prepared from the reaction of 13 g (0.1 mole) $(CH_3)_2SiCl_2$, 29.5 (0.2 mole) vinylmesitylene (mixture of isomers, n_D^{20} 1.5277), 4.5 g (0.65 g atom) lithium and 100 ml THF. The yield of the silacyclopentane was 15 g (42%, properties in Table 2, Figs. 2 and 3) and of the material which did not distil below 235° C (0.8 mm) was 12 g.

x, x'-Diphenyl-1, 1-x, x'-tetramethyl-1-silacyclopentane was prepared from $(CH_3)_2SiCl_2$, α-methylstyrene, and lithium in 30–50% yield (Table 1). The properties and IR spectra have been described previously [2] and the NMR spectrum is given in Fig. 2.

2, 3, 4, 5-Tetrapphenyl-1, 1-dimethyl-1-silacyclopentane was prepared, and some of its properties reported, previously in [2]. The H^1 NMR spectrum, given in Fig. 2, contains signals at τ 9.96 (CH_3 attached to Si), 6.78 (CH group), and a doublet at 2.99 and 3.12 (C_6H_5 groups in the 2, 5- and 3, 4- positions). The observed and calculated intensity ratios of these signals were 6.2 : 3.8 : 20 and 6 : 4 : 20, respectively.

x, x, x', x'-Tetraphenyl-1, 1-dimethyl-1-silacyclopentane was prepared by the addition of a mixture of 13 g (0.1 mole) dichlorodimethylsilane and 36 g (0.2 mole) 1, 1-diphenylethylene at 35–40° C over 20 min to 2.5 g (0.36 g atom) lithium in THF (100 ml) with vigorous stirring. The mixture was stirred for 2 hr, kept at ~ 20° for 20 hr, and then the deep-red color removed by addition of 1 ml methanol. After normal treatment, 9.7 g of a fraction with bp 236–238° C (0.7 mm) was obtained, and this crystallized on standing, mp 180.5–181.5° C (after five recrystallizations from ethanol with added water and acetone). The IR (Fig. 3) and NMR spectra (Fig. 2) confirm the presence of C_6H_5, CH_2, and CH_3 groups, and the ratios found from the NMR signals are close to the theoretical value of 20 : 4 : 6. The yield of nondistillable resin was 20 g.

x, x'-Diphenyl-1, 1-diethyl-1-silacyclopentane was prepared and some of its properties reported previously in [2]. The IR and NMR spectra are given in Figs. 3 and 2, respectively. The freezing point [−50° (glass)] and kinematic viscosity (ν^{20} 47.6 cst, ν^{50} 10.1 cst, and ν^{100} 2.5 cst) were determined for one fraction bp 165° (0.3 mm), d_4^{20} 1.5760.

x, x'-Ditolyl-1, 1-diethyl-1-silacyclopentane was obtained in an analogous manner from 15.7 g (0.1 mole) dichlorodiethylsilane, 23.6 g (0.2 mole) vinyltoluene, and 3 g (0.43 g atm) lithium in 70 ml THF (temperature ~ 0° C, addition 30 min, further stirring 60 min at ~ 20° C), to give a yield of 23.2 (72%). The properties and spectra are given in Table 2, Figs. 2 and 3. The yield of nondistillable polymer was 9 g.

1, x, x'-Triphenyl-1-methyl-1-silacyclopentane was prepared in 15.5 g (24%) yield from 38 g (0.2 mole) dichloromethylphenylsilane, 42 g (0.4 mole) styrene, and 4.5 g (0.65 g atom) lithium in 80 ml THF (~ 0° C, ~ 30 min). The properties and spectra are given in Table 2, Figs. 2 and 3. The nondistillable residue weighed 23.5 g.

x, x'-Ditolyl-1-Phenyl-1-methyl-1-silacyclopentane was prepared in 9 g (25.5%) yield, together with 26.1 g polymer, from 19 g (0.1 mole) $(C_6H_5)Si(CH_3)Cl_2$, 23.6 g (0.2 mole) vinyltoluene, 3 g (0.45 g atom) lithium in 50 ml THF (0° C, addition over 20 min, further stirring 1 hr) (see table 2, Figs. 2 and 3).

x, x'-Diphenyl-1-, 1-diallyl-1-silacyclopentane was obtained in 3.5 g (27%) yield from 7.5 g (0.04 mole) diallyldichlorosilane, 8.7 g (0.08 mole) styrene, and 3 g (0.43 g atom) lithium in 65 ml THF. The properties and elemental analysis (Table 2), and the IR and NMR spectra support the structure. The yield of residue with bp > 200° C (0.5 mm) was 9 g.

x, x'-Diphenyl-1-ethyl-1-silacyclopentane was prepared from 13 g (0.1 mole) dichloroethylsilane, 22 g (0.2 mole) styrene, and 3 g (0.45 g atom) lithium in 70 ml THF at −60 to −65° C with an addition time of 25 min and further stirring for 90 min at the same temperature. The yield was 5.4 g (20%) (Table 2). The IR and NMR spectra (Figs. 2 and 3) confirm the presence of the Si–H bond (absorption at 2130 cm^{-1} in the IR). The yield of polymer, which also contained the Si–H bond was 22.1 g.

The yield of the silacyclopentane was reduced to 15.5% when the reaction was carried but at −20° C, while at 20–30° C, the only product was a nondistillable polymer, mp 50–80° C, which according to the IR spectra contained almost no Si–H bonds.

The reaction of styrene and lithium with methyldichlorosilane under these conditions had similar results.

Acid hydrolysis of x, x'-diphenyl-1,1-dimethyl-1-silacyclopentane. A mixture of 13 g (0.05 mole) dimethyldiphenylsilacyclopentane [bp 152–153° (0.45 mm), d_4^{20} 1.0176, n_D^{20} 1.5769] and 14 g 91% H_2SO_4 (d 1.819) was agitated for 3 hr 45 min at 20° C. There was no gas evolution. The hydrolyzate was diluted with water, the organic layer washed with water, and aqueous Na_2CO_3, and dried over $MgSO_4$. Vacuum distillation gave 9.2 g (65%) sym-bis(x, x'-diphenylbutyl)-tetramethyldisiloxane, 253–258° (0.2 mm), n_D^{20} 1.5549, Found: C 78.24, 78.31; H 7.84, 7.92; Si 9.93, 10.06%. Calculated for $C_{36}H_{44}Si_2O$: C 78.78; H 8.08; Si 10.22%. The IR spectrum had an intense broad band at 1050 cm^{-1}, characteristic of the Si–O bond.

The authors express their sincere thanks to V. A. Shlyapochnikov, L. A. Leites, E. D. Lubuzh, V. I. Sheichenko, and S. V. Shlyapnikov for help in the spectroscopic and chromatographic analysis.

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7 December 1964

Zelinskii Institute or Organic Chemistry, AS USSR