PMR SPECTRA OF SOME FIVE- AND SIX-MEMBERED HETEROCYCLIC COMPOUNDS OF SILICON AND GERMANIUM*

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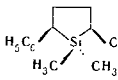
The PMR spectra of various 1-sila- and 1-germacyclopentanes and also those of some substituted disilacyclohexanes are discussed. The influence of the magnetic field of the aryl and vinyl substituents in 1,1-dialkyl-2,5-diaryl(vinyl)-1-sila(germa)cyclopentanes on the chemical shifts of the protons of the individual groups is studied, the differences found in the position of the PMR lines of the methyl and methylene groups showing the existence of cis-trans isomers in these heterocycles. With 1,1-dimethyl-2,5-divinylsilacyclopentane as an example, an increase in screening due to the magnetism of the multiple bonds for the protons of groups not directly connected with the unsaturated groupings and located in a direction perpendicular to the axis of the double bond has been found experimentally.

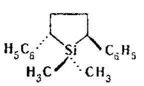
We have previously [1–3] described the preparation of di- and tetraaryl derivatives of 1,1-dialkyl(aryl)-1-sila(germa)cyclopentanes by the reaction of organyldichlorosilanes or -germanes and mono- or diarylethylenes, taken in a molar ratio of 1 : 2, with an excess of an alkali metal (usually lithium) in tetrahydrofuran (THF). Similarly, from RR'$SiCl_2$ and 1,3-dienes (in a molar ratio of 1 : 2) we have obtained bis-vinyl-substituted 1,1-diorganyl-1-silacyclopentanes [4]. Using an equimolar ratio of RR'$SiCl_2$ and an arylethlene, with the simultaneous dilution of the THF with a hydrocarbon solvent, we have obtained aryl-substituted disilacyclohexanes [5].

Although the structure of the five-membered heterocycles obtained in this way as 1-sila- or 1-germacyclopentanes has been demonstrated [1–4] by their analysis and a study of their physicochemical properties, the positions of the aryl or vinyl substituents had not been definitively elucidated until recently. In particular, the results of a gas-chromatographic analysis and the PMR spectrum of the 1,1-dimethyl-x,x'-diphenyl-1-silacyclopentane formed from styrene and $(CH_3)_2SiCl_2$ (2 : 1) has shown the presence in this compound of at least two isomers, which could be connected with different positions of the C_6H_5 group either in relation to the plane of the silacyclopentane ring (cis-trans isomerism) or relative to the silicon atom (position isomerism) [2]. A similar pattern has been observed in the case of other aryl-substituted 1,1-diorganyl-1-silacyclopentanes and the corresponding germa compounds [2, 6].

With the aid of independent synthesis, chemical reactions, and UV and PMR spectra, we have recently [7] shown that the five-membered heterocycles formed from arylethylenes and RR'MCl_2 (M = Si or Ge) at a molar ratio of 2 : 1 consist exclusively of 2,5-diaryl-1,1-diorganyl-1-sila(germa)cyclopentanes (mixtures of cis and trans isomers), for example:



cis isomer



trans isomer

This conclusion is in harmony with recent data [8, 9] on the structure of the dimethyldiphenylsilacyclopentane obtained similarly from $(CH_3)_2SiCl_2$ and styrene (1 : 2).

In this paper we consider in detail the PMR spectra of a number of aryl-substituted 1,1-diorganyl-1-silacyclopentanes, 1,1-diorganyl-1-germacyclopentanes, 1,1,4,4-tetraorganyl-1,4-disilacyclohexanes, and some other similar heterocycles. In considering the PMR spectra of these compounds, which are given in Fig. 1, some of them having been given previously [2, 6], we were primarily interested in the dependence of the positions of the signals of particular groups of protons on the structure and isomeric composition of the heterocycles studied and the possibility of the use of PMR data to establish the structure of similar heterocycles studied and the possibility of the use of PMR data to establish the structure of similar heterocyclic compounds.

A consideration of the spectra of the 2,5-diaryl-substituted 1,1-dimethyl-1-sila(germa)cyclopentanes (see table and figure) show that the presence in them of magnetically anisotropic substituents—aryl groups possessing dissimilar magnetic susceptibilities in different directions [10]—has a substantial effect on the values of the chemical shifts, τ, of the CH_3 groups attached to silicon or germanium. At the same time, as was to be expected, this influence is shown unequally for the cis and trans isomers. Thus, in place of one signal of the protons of the CH_3 groups in the unsubstituted 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (I) with τ 9.91 ppm, in the spectrum of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane (II) three lines appear with τ = 9.75, 10.15, and 10.65 ppm and with a ratio of intensities of 1 : 2 : 1. The same pattern is found for similar germanium compounds, as is well seen from a comparison of the spectra of XI (τ_{CH_3} 9.76 ppm) and XII (τ_{CH_3} 9.58, 9.92, and 10.43 ppm).

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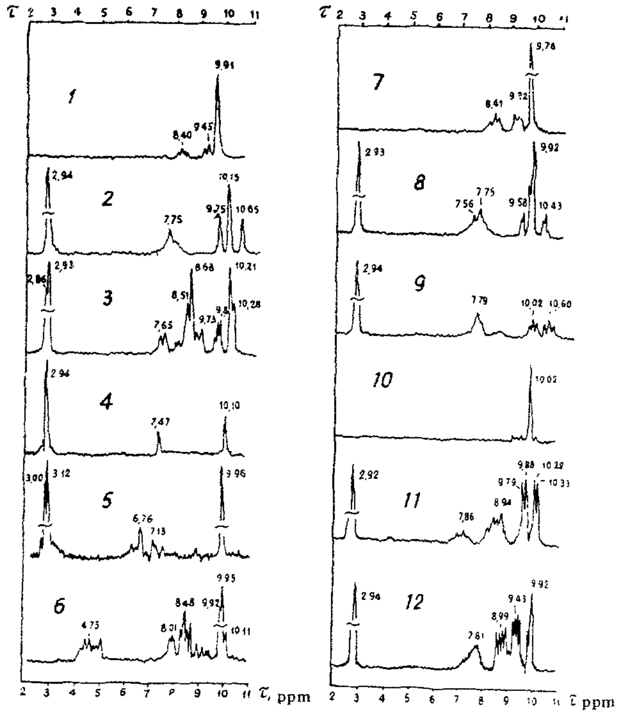
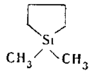
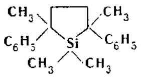
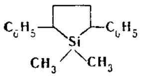
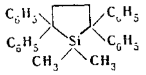
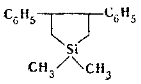
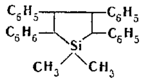
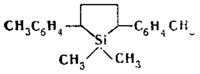
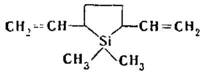
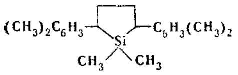
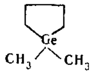
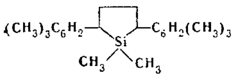
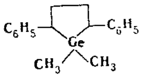
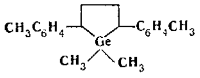


PMR spectra of silicon- and germanium-containing heterocycles: 1) 1, 1-dimethyl-1-silacyclopentane (I); 2) 1, 1-dimethyl-2, 5-diphenyl-1-silacyclopentane (II); 3) 1, 1, 2, 5-tetramethyl-2, 5-diphenyl-1-silacyclopentane (VII); 4) 1, 1-dimethyl-2, 2, 5, 5-tetraphenyl-1-silacyclopentane (VIII); 5) 1, 1-dimethyl-2, 3, 4, 5-tetraphenyl-1-silacyclopentane (IX); 6) 1, 1-dimethyl-2, 5-divinyl-1-silacyclopentane (X); 7) 1, 1-dimethyl-1-germacyclopentane (XI); 8) 1, 1-dimethyl-2, 5-diphenyl-1-germacyclopentane (XII); 9) Di-(1-methyl-2, 5-diphenyl-1-silacyclopent-1-yl) (XIII); 10) 1, 1, 4, 4-tetramethylbis(trimethylsilyl)-1, 4-disilacyclohexane (XIV); 11) Diphenyl-1, 1, 4, 4-tetramethyl-1, 4-disilacyclohexane (XV); 12) 1, 1-diethyl-2, 5-diphenyl-1-silacyclopentane (XVI).

Chemical Shifts for the CH_3 Groups Attached to Silicon or Germanium

Compound		τ, ppm	Compound		τ, ppm
	(I)	9.91		(VII)	10.28: 10.21 and $\sim$9.75
	(II)	10.65: 10.15 and 9.75		(VIII)	10.10
	(III)	9.73[9]		(IX)	9.96
	(IV)	10.61: 10.18 and 9.75		(X)	10.11: 9.95 and 9.92
	(V)	10.16: 9.92 and $\sim$9.70		(XI)	9.76
	(VI)	10.06: 9.93 and 9.81		(XII)	10.43: 9.92 and 9.58
				(XIIa)	10.48: 9.86 and 9.57

A comparison of the spectra of II and XII taken at 30, 40, and 60 MHz clearly shows that all three resonance signals belong to different types of protons (different CH groups).

The observed anomalously remote shift of the signals of the CH_3 groups of compounds II and XII is due to the fact that the methyl groups, being located in the space above the plane of the benzene rings, which are apparently arranged approximately perpendicularly to the plane of the five-membered heterocycle, undergo a strong screening action from the direction of the magnetic field of the aromatic rings induced by the motion of the π-electrons. The methyl groups of the trans isomers of II and XII present in this additional magnetic field remain practically equivalent, since the nonplanarity of the five-membered heterocycles is usually extremely small. In view of this, the trans isomers of II and XII show only one strong signal of the protons of the CH_3 groups at τ 10.15 and 9.92 ppm, respectively. In the cis isomers of II and XII, one of the methyl groups is present, essentially, between two benzene nuclei and is subject to the maximum screening action, which causes a shift of signals of these CH_3 groups into the strongest field (τ 10.65 and 10.43 ppm, respectively). The influence of the additional magnetic field of the benzene rings on the second CH_3 groups of the cis isomers, acting in the opposite direction from the CH_3 groups, is considerably less and, in fact, is in the reverse direction. This leads to a small shift in the resonance lines of the CH_3 groups in the weak-field direction (signals at τ 9.75 ppm for II and 9.58 ppm for XII). A similar value of τ (9.73 ppm) is observed for the protons of the CH_3 groups of 1,1-dimethyl-3,4-diphenyl-1-silacyclopentane (III) [9], where the mutual influence of the C_6H_5 and CH_3 groups must evidently be very small.

gives a ratio of trans and cis isomers of ~50 : 50 for II and ~60 : 40 for XII, which agrees with the results of their chromatographic analysis [2, 6].

When, instead of two, four C_6H_5 groups are present in the 1,1-dimethylsilacyclopentane ring (compounds VIII and IX, table), in their PMR spectra only one signal of the protons of the CH_3 groups remains, with τ 10.10 ppm for VIII* and 9.96 ppm for IX. This shows the equivalence of the CH_3 groups in VIII and IX and, consequently, the transoid and symmetrical arrangement of the phenyl substituents in positions 2 and 5 of these heterocycles which, of course, is the most sterically favorable arrangement.

The introduction of one CH_3 group into each of the benzene nuclei of II and XII, i.e., the passage from II to IV and from XII to XIIa does not in fact change the number, position, and ratio of the signals of the protons of the $(CH_3)_2Si$ and $(CH_3)_2Ge$ groupings. However, the further replacement of hydrogen atoms of the aryl substituent by CH_3 groups obviously causes a change in the mutual orientation of the former and, as a consequence, a considerable displacement of the signals of the CH_3 groups attached to silicon in the weak-field direction—the displacement $\Delta\tau$ amounts to 0.5–0.7 ppm on passing from II and IV to V and VI (see table and [2]). A similar but smaller displacement of the signals of the CH_3 groups attached to silicon is brought about by the replacement of one of them in II and IV by a phenyl group ($\Delta\tau$ ~0.3 ppm) [2].

The replacement of the methine protons of the silacyclopentane ring by CH_3 groups, i.e., the passage from II to VII, is shown in the disappearance (or a displacement in the weak-field direction) of the most remote lines of the CH_3 groups on the silicon atom (in the 10.6 ppm region). Simultaneously there is an increase in the intensity and a complication of the form of the methyl line located in the lowest fields (about 9.7 ppm). It must apparently be considered that here, also, there is a change in the orientation of the benzene rings and, consequently, a change in the topography of the magnetic field induced by them.

The presence of a large number of massive substituents in the bis(silacyclopentyl) XIII leads to the situation that the methyl groups inevitably come into the field of action of some or all of the benzene nuclei. As a result, two groups of lines appear in the spectrum with centers at about 10.0 and 10.6 ppm (including one line with a record displacement, $\tau \sim 10.8$ ppm), while their complex nature may indicate the existence of different forms of screening. However, in contrast to the majority of the silacyclopentanes considered, there are no signals in the 9.7–9.8 ppm region.

The specific influence of aryl substituents on the position and nature of the signals of the CH_3 groups attached to silicon is also clearly shown in a comparison of the structurally similar disubstituted Si-tetramethyldisilacyclohexanes XIV and XV (see figure). The single line with τ 10.02 ppm from all the methyl groups of compound XIV is replaced in the case of XV by two doublets. At the same time, all four lines are chemical shifts, as was shown by a comparison of the spectra taken at 30 and 40 MHz.

A consideration of the positions of the lines of the methylene and methine protons of these heterocycles give interesting and important information. A characteristic feature is the presence in the spectra of a majority of the diaryl-substituted 1,1-dimethylsila(germa)cyclopentanes (II, IV–VI, XII, and XIIa) of practically a single common signal for the protons of the CH and CH_2 groups of the heterocyclic ring in the region of comparatively low fields, 7.5–7.8 ppm. Thus, a superposition of the protons of the CH groups connected with silicon or germanium on the signals of the protons of the CH groups connected with silicon or germanium on the signals of the protons of the CH_2 groups of the ring not connected with the heteroatom is found. This marked displacement of the signals of

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*In the PMR spectrum of compound VIII [2], in addition to the actual line for the CH_3 groups with τ 10.10 ppm, two other lines have been shown erroneously—with τ ~10.0 and 9.68 (printed as 8.68) ppm and for the CH_2 groups of the heterocycle, in addition to the actual signal at τ 7.4 ppm, low-intensity signals of impurities at τ 7.98 and 6.17 ppm.

the protons of the heterocyclic ring in the weak-field direction (by 0.5–0.7 and 1.5–1.7 ppm as compared with the similar signals of the unsubstituted heterocycles I and XI) is in complete agreement with the proved [7–9] 2, 5-position of the aryl substituents in compounds II, IV–VI, XII, and XIIa and with the approximately perpendicular orientation of the planes of the benzene ring relative to the plane of the heterocycles. In actual fact, in the case of the isomeric dimethyldiphenylsilacyclopentane III with a 3, 4-arrangement of the C_6H_5 groups, different signals are observed for the protons of the $SiCH_2$ and C_6H_5CH groupings of the heterocycle (multiplets at 8.8 and 7.1 ppm, respectively) [9]. A similar multiplet in the 8.3–8.9 ppm region is found in the spectrum of compound XV which also has $SiCH_2$ groupings (see figure). At the same time, as was to be expected, the intensity of the signals of these methylene groupings is approximately double that of the lines of the methine protons located in the 7.5–7.9 ppm region.

A marked difference in the positions of the signals of the α- and β-CH groups of the heterocyclic ring (relative to the Si atom) is also observed for 1, 1-dimethyl-2, 3, 4, 5-tetraphenylsilacyclopentane (IX) (see figure). The position of the signal of the protons of the β-CH groups (6.8 ppm) is, as was to be expected, fairly close to the position of the signal of the similar CH groups of III (7.1 ppm) [7]. Furthermore, in the spectrum of IX there is also a difference in the signals of the C_6H_5 groups located in the α (2, 5-) and β (3, 4-) positions of the heterocycle—the difference in the chemical shifts, $\Delta\tau$, is 0.12 ppm.

The PMR lines for the acyclic $SiCH_2$ and CCH_3 groupings are generally located in the regions about 9.4 and 9.0 ppm, respectively. However, in the spectrum of the diphenyl-substituted 1, 1-diethylsilacyclopentane XVI, which obviously consists of a mixture of cis and trans isomers, signals in the stronger field, from 8.9 to 9.9 ppm, are also observed for these protons, which is again a consequence of the screening influence of the neighboring benzene rings. Furthermore, a coincidence of the chemical shifts of the protons of the cyclic SiCH and CCH_2 groupings in the heterocycles II and VI (a single complex signal at ~7.8 ppm) must be mentioned.

Magnetic anisotropy of a different type appears in the spectrum of the di(vinyl-substituted) 1, 1-dimethyl-1-silacyclopentane X. A comparison of the spectrum of this compound and that of the unsubstituted 1, 1-dimethylsilacyclopentane (I) shows that the lines of the CH_3 groups of X undergo a small displacement from the 9.91 ppm region and are converted into three lines with τ 9.92, 9.95, and 10.11 ppm (see figure). This displacement is a consequence of a screening action on the CH_3 groups on the part of the vinyl radicals. In actual fact, the double carbon-carbon bond possesses different magnetic susceptibilities in three directions: a minimum in the direction of prolongation of the double bond, a maximum in a direction transverse to the bond and lying in the plane of the bond, and an intermediate value in the direction transverse to the bond but perpendicular to this plane. The result of the decrease in the total magnetic field for the protons located in the direction of the prolongation of the double bond, i. e., protons of the $>C{=}\underset{|}{C}{-}CH_2{-}$ and, particularly, the $>C{=}\underset{|}{C}{-}H$, type, is a displacement of their signals in the direction of lower values of τ as compared with the saturated compounds. However, the effect of the increased screening in the direction transverse to the double bond is an unusual phenomenon.

EXPERIMENTAL*

The PMR spectra were obtained on a high-resolution (10^{-8}) radiospectrometer of the JNM-3 type at a frequency of 40 MHz at room temperature. The solvent used was CCl_4 (concentration of the solutions 20–40%) and the internal standard (~1%) tetramethylsilane (τ 10.00 ppm) or tetramethylgermane (τ 9.87 ppm). The chemical shifts were determined by the side-band method.

1, 1-Dimethyl-1-silacyclopentane (I) was obtained [11] from 1, 4-dibromobutane, magnesium, and dimethyldichlorosilane in ether; yield 57%, bp 104° C (752 mm), n_D^{20} 1.4350, d_4^{20} 0.7933. According to the literature [11], bp 106° C (760 mm), n_D^{20} 1.43487, d_4^{20} 0.7938.

1, 1-Dimethyl-1-germacyclopentane (XI). A solution of 100 g (0.46 mole) of 1, 4-dibromobutane in 100 ml of ether was added dropwise to 36 g (1.5 g-at) of magnesium in 250 ml of ether. After the mixture had been boiled for 2 hrs the ether was distilled off to dryness and replaced by 200 ml of THF. Then, with vigorous stirring, 53 g (0.31 mole) of dimethyldichlorogermane in 75 ml of THF was added dropwise. After the mixture had been boiled for 3 hr, the liquid reaction products were decanted off and distilled through a column. The yield of 1, 1-dimethylgermacyclopentane with bp 118–119° C (752 mm), n_D^{20} 1.4595, d_4^{20} 1.0641, was 16.8 g (35%). Found, %: C 44.77, 44.86; H 8.78, 8.76; Ge 46.70, 46.61. Calculated for $C_6H_{14}Ge$, %: C 45.39; H 8.89; Ge 45.72. Raman spectrum ($\Delta\nu$, cm^{-1}): 153 (1), 167 (1), 191 (2 broad), 284 (0), 342 (5), 475 (2), 544 (0), 574 (10), 603 (2), 623 (1), 698 (1), 851 (3), 953 (1), 1032 (1), 1075 (1), 1113 (0), 1143 (2 broad), 1202 (1 broad), 1246 (2 broad), 1322 (0), 1416 (2), 1450 (2), 2855 (7), 2879 (1), 2911 (10), 2938 (3), 2959 (2), 2979 (3).

The syntheses and properties of the aryl- and vinyl-substituted silacyclopentanes [1, 2, 4], of the substituted disilacyclohexanes [5], and of the diaryl-1, 1-dimethylgermacyclopentanes [3] have been reported previously.

Bis(1-methyl-2, 5-diphenyl-1-silacyclopentyl) (XIII). A mixture of 30 g (0.2 mole) of CH_3SiCl_3 and 42 g (0.4 mole) of styrene was added with vigorous stirring, using a steel turbine stirrer, to 5 g (0.7 g-at) of small pieces of lithium in 100 ml of THF (~40° C, 40 min). After further stirring (20–30° C, 1 hr) and the usual working up, three vacuum distillations yielded 11.5 g (23%) of the bis(dimethyldiphenylsilacyclopentyl). Viscous liquid with bp 270–272° C (0.45 mm), n_D^{20} ~1.600. It crystallized on standing, mp 174–175° C (from CCl_4). Found, %: C 81.26, 81.16; H 8.05, 8.01; Si 9.98, 10.17; mol. wt. 484, 489 (cryoscopically in benzene). Calculated for $C_{34}H_{38}Si_2$, %: C 81.22; H 7.62; Si 11.16; mol. wt. 502.8.

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