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Abstract

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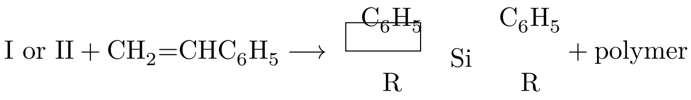
ON THE MECHANISM OF THE FORMATION OF ARYL-SUBSTITUTED SILACYCLOPENTANES FROM ORGANODICHLOROSILANES, STYRENES, AND LITHIUM

A NEW METHOD FOR THE PREPARATION OF SUBSTITUTED DISILACYCLOHEXANES

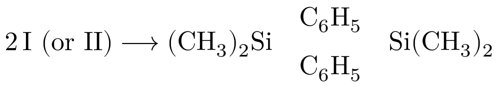
Earlier we ([1]) found a new general method for obtaining aryl-substituted silacyclopentanes (yields up to 80%), consisting in the interaction of organodichlorosilanes and styrenes (molar ratio 1 : 2) with metallic lithium (sodium) in tetrahydrofuran (THF). In this case the formation was assumed of intermediate biradicals of the type $C_6H_5\dot{C}HCH_2\dot{S}iR_2$ (I) or of the corresponding bions $C_6H_5\overset{-}{C}HCH_2\overset{+}{S}iR_2$ (II), which, reacting with styrene, led to substituted silacyclopentanes and silicon-hydrocarbon polymers, for example



$$\text{I or II} + CH_2{=}CHC_6H_5 \longrightarrow \begin{array}{c} C_6H_5 \\ \boxed{} \\ R \end{array} Si \begin{array}{c} C_6H_5 \\ \\ R \end{array} + \text{polymer}$$

However, no products of dimerization of such intermediate biradicals or bions, confirming the correctness of the proposed mechanism, were isolated by us in any of the experiments carried out earlier. This could be explained by the presence in all experiments of an excess of styrene, which caused the preferential interaction of I or II with it.

Assuming that decreasing the amount of styrene used to an equimolar amount (relative to R_2SiCl_2) and the use of an inert, for example hydrocarbon, diluent should reduce the probability of addition of the proposed biradical (I) or bion (II) to styrene, we undertook the present investigation. Indeed, when $(CH_3)_2SiCl_2$ and styrene were used in a molar ratio of 1 : 1 and THF was diluted with *n*-heptane (volume ratio 1 : 1), we obtained the dimer I or II—X,X′-diphenyl-1,1,4,4-tetramethyl-1,4-disilacyclohexane (a mixture of two isomers) in a yield of 30% of theory:

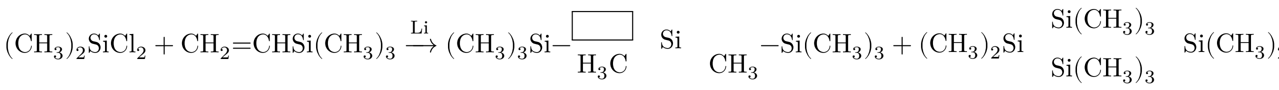


$$2\,\text{I (or II)} \longrightarrow (CH_3)_2Si \begin{array}{c} C_6H_5 \\ \\ C_6H_5 \end{array} Si(CH_3)_2$$

Fig. 1. IR spectra of substituted disilacyclohexanes

Figure 1: Fig. 1. IR spectra of substituted disilacyclohexanes

Similar disilacyclohexanes were formed under the above conditions from styrene and other organodichlorosilanes, and also from $(CH_3)_2SiCl_2$ and α-methylstyrene or stilbene (yields 5-30%). In addition, bis-trimethylsilyl-substituted 1,1,4,4-tetramethyl-1,4-disilacyclohexane (yield $\sim$ 20%) was obtained by us, together with the corresponding silacyclopentane, from dimethyldichlorosilane, vinyltrimethylsilane, and lithium under analogous conditions:



$$(CH_3)_2SiCl_2 + CH_2{=}CHSi(CH_3)_3 \xrightarrow{Li} (CH_3)_3Si-\underset{H_3C}{\boxed{}}\ Si\ \underset{CH_3}{}-Si(CH_3)_3 + (CH_3)_2Si\ \overset{Si(CH_3)_3}{\underset{Si(CH_3)_3}{}}\ Si(CH_3)$$

The correctness of the structure assigned to the isolated organosilicon compounds follows from the data of their elemental analysis, cryoscopic determination of molecular weights, and also from their physical and chemical properties. In particular, these compounds did not change on heating to 50° with saturated aqueous or alcoholic KOH solution or with moist piperidine, which indicates the absence in them of Si–Si bonds and, consequently, rules out the possibility of a 1,2-disilacyclohexane structure for them.

Fig. 1. IR spectra of substituted disilacyclohexanes

In addition, the structure of the substituted 1,4-disilacyclohexanes synthesized by us is confirmed by the data of IR spectra* (Fig. 1) and high-resolution NMR spectra. Finally, the crystallinity and rather high melting point of the simplest of the disilacyclohexanes obtained also confirm their structure.

Thus, the data obtained may be regarded as evidence for the intermediate participation, in the reactions of formation of aryl-substituted silacyclopentanes, of biradicals or biions similar to I and II. The formation of the latter, in turn, apparently occurs either by direct addition of the carbeneoid $R_2Si:$ formed as an intermediate to styrene, or as a result of interaction of the starting R_2SiCl_2 with the lithium adduct to styrene, for example:

$$\begin{array}{lll} \text{(A)} \quad R_2SiCl_2 \xrightarrow[\text{THF}]{2Li} R_2Si(Li)Cl \xrightarrow{-LiCl} R_2Si: & \xrightarrow{CH_2=CHC_6H_5} & \\ & & \longrightarrow \text{I or II.} \\ \text{(B)} \quad C_6H_5CH{=}CH_2 \xrightarrow{2Li} C_6H_5CH(Li)CH_2Li & \xrightarrow[-2Li\cdot Cl]{R_2SiCl_2} & \end{array}$$

In favor of path (B), in addition to the previously noted (^{1}) ease of addition of alkali metals to styrene, there also speaks the fact of formation of silacyclopentanes from styrene, dimethyldichlorosilane, and lithium in hydrocarbon media with small additions of THF, in which $(CH_3)_2SiCl_2$ itself reacts only very weakly with metallic lithium. On the other hand, the feasibility of path (A) is confirmed by the exceptional ease of interaction of R_2SiCl_2 with lithium in THF, which apparently does indeed lead to silylenes $R_2Si :$. At the same time, the possibility of addition of the latter to unsaturated compounds is quite firmly established. In particular, dimethylsilylene $(CH_3)_2Si :$ adds to toluene ([2]), and also to ethylene, isobutylene, 1-heptene, cyclohexene, and other similar olefins ([3]), which are practically inert toward lithium and its compounds under the conditions adopted by us.

Both of the above-mentioned paths (organometallic and carbeneoid) are also feasible in the case of vinyltrimethylsilane, which, according to our observations, readily adds lithium in THF, and, according to literature data ([4]), is very active also in free-radical addition reactions at the multiple bond.

* Taken by L. A. Leites on a UR-10 spectrometer in a "solid solution" of KBr.

Experimental Part

All experiments were carried out, as before (1), with vigorous stirring of the reaction mixture by a steel mechanical turbine-type stirrer in an atmosphere of dry purified nitrogen. The end of the reaction was established by the disappearance of hydrolyzable chlorine in the reaction products.

X,X′-Diphenyl-1,1,4,4-tetramethyl-1,4-disilacyclohexane. To 4.5 g (0.65 g-atom) of small pieces of lithium in 40 ml of THF there was added dropwise a mixture of 26 g (0.2 mole) of dimethyldichlorosilane, 21 g (0.2 mole) of styrene, 40 ml of THF, and 80 ml of dry *n*-heptane (~20°, 1 hr). After completion of the reaction, the products were filtered off from excess lithium and its chloride; the filtrate was evaporated in vacuo and distilled. There were obtained 9.8 g (30%) of white crystals which, after three recrystallizations from aqueous ethanol, melted at 160–161° and, according to gas-liquid chromatography (GLC), were a mixture of two isomers in a ratio of ~1:1 (column 2 m × 4 mm with 15% polyethylene glycol sebacate on Chromosorb, 210°; carrier gas—helium).

Found, %: C 74.27, 73.99; H 8.65, 8.60; Si 16.79, 17.05
$C_{20}H_{28}Si_2$. Calculated, %: C 74.01; H 8.70; Si 17.29

Mol. wt.: found (cryoscopically in C_6H_6) 313; calculated 324.5. Subsequent threefold crystallization of the product with m.p. 160–161° from ethanol with addition of acetone made it possible to isolate one of the isomers in pure form (according to GLC), m.p. 164°. The disilacyclohexane obtained (m.p. 160–161°) did not evolve hydrogen on heating to 50° for 1 hr with saturated aqueous or alcoholic KOH solution or with moist piperidine.

Formation of the same diphenyltetramethyldisilacyclohexane was also observed when *n*-heptane in this experiment was replaced by other inert hydrocarbons.

X,X′-Bis-trimethylsilyl-1,1,4,4-tetramethyl-1,4-disilacyclohexane. In a similar manner, at 20–25°, from 4.6 g (0.65 g-atom) of lithium, 26 g (0.2 mole) of dimethyldichlorosilane, and 20 g (0.2 mole) of vinyltrimethylsilane (b.p. 55–56°, n_D^{20} 1.3906) in 160 ml of a mixture of THF and *n*-heptane (1:1), there were obtained 6 g (19%) of white crystals with m.p. 89–89.5° (from aqueous C_2H_5OH), which, according to GLC, were an individual compound.

Found, %: C 53.72, 53.75; H 11.52, 11.57; Si 34.81, 34.95
$C_{14}H_{36}Si_4$. Calculated, %: C 53.09; H 11.47; Si 35.44

Mol. wt.: found (cryoscopically in C_6H_6) 331, 313; calculated 316.7.

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

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