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RADICAL IONS

XXVI *. RADICAL ANIONS OF PERPHENYLCYCLOPOLYSILANES

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Summary

Perphenylcyclopolysilanes $[Si(C_6H_5)_2]_n$ ($n = 4, 5$) are reduced by potassium to radical anions. Their simple ESR spectra demonstrate, that the extra electron is confined to the inner Si_nC_{2n} skeleton of the uncleaved and presumably planarized cyclopolysilanes.

Introduction

One of the most striking properties of cyclopolysilanes is their reducibility to form radical anions, in which the extra electron is delocalized predominantly over the polysilane ring [2—4]. Although several radical anions of permethylcyclopolysilanes $[Si(CH_3)_2]_n^{\cdot-}$ with $n = 4,5$ and 6 have been investigated by electron spin resonance (ESR) spectroscopy, the corresponding, sterically overcrowded perphenyl-substituted derivatives have attracted no attention **. We present below the results of a study of the one-electron reduction of perphenylcyclopolysilanes $[Si(C_6H_5)_2]_n$ either with potassium metal or electrolytically in solutions of THF/DME containing tetrabutylammonium perchlorate:

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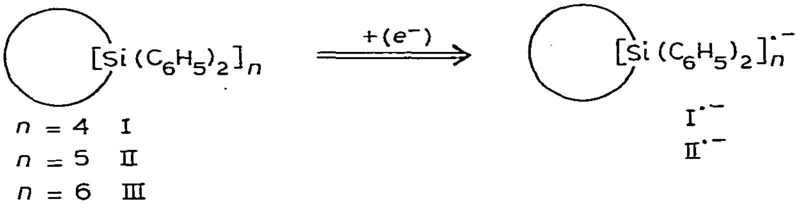
* For part XXV see ref. 1.

** Some monophenyl derivatives, such as phenylnonamethylcyclopentasilane and phenylundecamethylcyclohexasilane, have been reduced to the corresponding radical anions [3]. The ESR data are of interest, because they demonstrate that the extra electron enters preferentially the polysilane ring and not the phenyl π-system.



One-electron reductions and discussion of the radical anion ESR spectra

Octaphenylcyclotetrasilane

The radical anion $I^{\cdot -}$ is formed on reduction with K in a 1/1 mixture of THF/DME at temperatures between 173 K and 200 K. The radical anion is slightly yellow, and its recorded simple ESR spectrum consists of only 5 lines: a singlet with 2 doublet satellites (Fig. 1). The line widths of the broad ESR central line amounts to 0.13 mT. The outer and inner doublets are attributed to splittings by the isotopes ^{13}C (I 1/2, natural abundance 1.1%) and ^{29}Si (I 1/2, natural abundance 4.7%). For ^{13}C (8 equivalent carbon atoms) each wing of the doublet should have 4.4% of the total intensity, whereas for ^{29}Si (4 equivalent silicon atoms) an intensity of 9.4% is predicted. The observed intensities amount to 4% and to 9.5%, respectively, and therefore the outer doublet is assigned to ^{13}C of the phenyl ring α-carbons and the inner one to ^{29}Si. Splittings due to the phenyl ring protons must obviously be smaller than 0.01 mT. In contrast to the reaction with potassium, the electrochemical reduction of $Si_4(C_6H_5)_8$ failed even in the same solvent mixture (THF/DME, 1/1) and at low temperatures: no ESR signals could be detected.

Decaphenylcyclopentasilane

Reduction to its radical anion $II^{\cdot -}$ can be achieved both by potassium metal and electrochemically. The ESR spectrum of $II^{\cdot -}$ is rather similar in its overall appearance to that of the four-membered ring derivative $[Si(C_6H_5)_2]_4^{\cdot -}$ (Fig. 1), although expectedly significant differences in the coupling constants of the doublet satellites are observed (Table 1). Potassium reduction at temperatures above 200 K yielded an ESR spectrum, in which the lines of both radical anions $I^{\cdot -}$ and $II^{\cdot -}$ are superposed. After warming to room temperature, the ESR spectrum changed to that of a phenylsilylbenzene radical anion [5] *, consisting of a doublet (0.83 mT) and of a triplet (0.28 mT). On the other hand, electrolytic reduction of II in THF/DME (1/1) using tetra-n-butyl ammonium perchlorate as the supporting electrolyte produced only the ESR spectrum of $II^{\cdot -}$ without contamination by $I^{\cdot -}$. The ESR spectrum disappeared rapidly at temperatures above 210 K.

Dodekaphenylcyclohexasilane

All the various attempts to reduce III to its radical anion $III^{\cdot -}$ have been un-

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* For example, the phenyltrimethylsilane anion radical shows splittings of a doublet (0.809 mT) and two triplets (0.265 and 0.106 mT) due to *para*, *ortho*- and *meta*-protons, respectively.

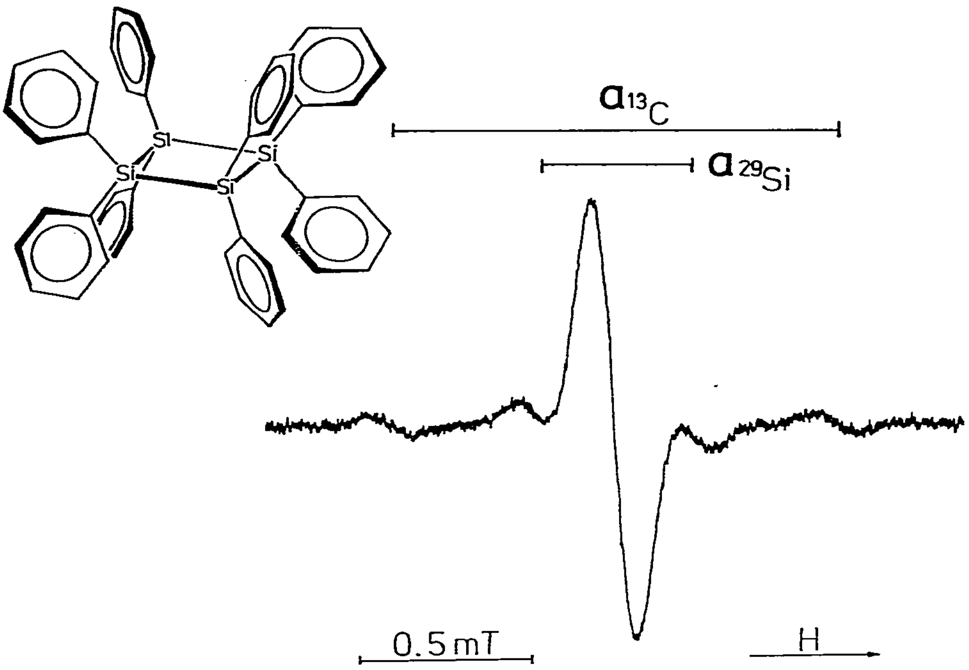

Fig. 1. ESR spectrum of the octaphenylcyclotetrasilane radical anion $I^{\cdot-}$ at 190 K in THF/DME (1/1).

TABLE 1

ESR PARAMETERS FOR PERPHENYLPOLYSILANE RADICAL ANIONS $I^{\cdot-}$ AND $II^{\cdot-}$

Radical anion	Colour	*g*-Value	Splitting constants (mT)		
			$a_{^{29}Si}$	$a_{^{13}C}$	a_H
$[Si(C_6H_5)_2]_4^{\cdot-}$	yellow	2.0046	0.44	1.31	<0.01
$[Si(C_6H_5)_2]_5^{\cdot-}$	yellow	2.0046	0.36	1.00	<0.007

successful so far because of the insolubility of III in most solvents or their mixtures.

Conclusions

The radical anions both of the four- and five-membered perphenylpolysilane rings are stable at low temperatures. The reduction is accompanied neither by the well-known cleavage of perphenylated Si—Si bonds [6] nor by complete further reduction to secondary anion radicals such as occurs in the reaction of polyphenylsilanes with metals [7].

Most interesting, however, is the comparison of the perphenylated with the permethylated [2—4] polysilane radical anions. The larger *g*-values determined for the phenyl derivatives (Table 1) relative to the methyl substituted ones ($g_{Si_4R_8^{\cdot-}}$ = 2.0038 and $g_{Si_5R_{10}^{\cdot-}}$ = 2.0032 [3]), indicate a higher spin density in their Si_n skeleton. On the other hand and in contrast to the permethylated radical anions, no hydrogen coupling hyperfine structure can be resolved in the ESR spectra reported (Fig. 1 and Table 1). This observation suggests that the extra electron does not enter the phenyl rings, and rather is delocalized within the Si_n ring and the surrounding cylinder of the $2n$ phenyl ring α carbons. As expected, the spin density in each SiC_2 moiety decreases with increasing ring size as illustrated by the individual ^{29}Si and ^{13}C coupling constants (Table 1). If multiplied for unit spin density $n \times a_{^{29}Si}$ and $2n \times a_{^{13}C}$ the resulting values for the four-membered radical anion $0.44 \times 4 = 1.76$ mT and $1.31 \times 8 = 10.48$ mT, agree quite well with those for the five-membered one, $0.36 \times 5 = 1.80$ mT and $1.00 \times 10 = 10.00$ mT, respectively. From this comparison it may be tentatively concluded that the ring structures of both radical anions, $[Si(C_6H_5)_2]_4^{\cdot-}$ and $[Si(C_6H_5)_2]_5^{\cdot-}$ are similar, and possibly planar.

Experimental part

Radical anion generation was carried out by the standard procedure using sublimed alkali metal under high vacuum. For the electrolytic reduction intra muros the apparatus described in ref. 8 was used.

Electron spin resonance spectra were recorded with a Varian E 9 equipment (frequency 9.5 GHz, 330 mT magnetic field and field modulation 100 kHz), and calibrated with perylene radical anion in DME : a_H 0.04503 mT, 0.30473 mT, 0.34934 mT and g 2.002656 [9].

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