ORGANOSILICON IMINOXYL POLYRADICALS*

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One of us has already published on the synthesis of the first iminoxyl tri- and tetraradicals [1]. A study of their solutions by the EPR method led to the discovery of the phenomenon of electronic interaction of the paramagnetic centers [2].

The present communication is devoted to the synthesis and study of the EPR spectra of previously unknown individual tetra-, penta- and hexaradicals. The synthesis of the polyradicals were effected by a single scheme — the reaction of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl [3, 4] with appropriate organochlorosilanes in an inert solvent medium with addition of triethylamine. We prepared the 1,2-bis(methyldichlorosilyl)ethane [5]; 1,2-bis(methyldichlorosilyl)ethylene [6]; 1,2-bis(phenyldichlorosilyl)ethylene [7]; 1-methyldichlorosilyl-3-trichlorosilylpropane [5]; bis(trichlorosilyl)methylene [9]; 1,2-bis(trichlorosilyl)ethane [5]; 1,2-bis(trichlorosilyl)ethylene [10, 7]; 1,3-bis(trichlorosilyl)propane [11] and 1,4-bis(trichlorosilyl)benzene [12], intended for synthesis of the polyradicals, by previously described methods. For 1-methyldichlorosilyl-2-phenyldichlorosilylethane and 1,2-bis(phenyldichlorosilyl)ethane [13], we used the Speier method [14] of hydrosilylation in the presence of a catalyst for the first time. In distinction from the hydrosilylation of vinyltrichlorosilane or methylvinyldichlorosilane with the comparatively unavailable dichlorosilane [15], the synthesis of 1,1,1,4,4,7,7,7-octachlorotrisilylethylene and 1,1,4,4,7,7-hexachloro-1,7-dimethyltrisilylethylene was accomplished by hydrosilylation of divinyldichlorosilane with the appropriate hydridosilane. Phenylvinyldichlorosilane was prepared analogously to methylvinyldichlorosilane [16] by a high-temperature condensation method according to the scheme

$$\mathrm{PhCl_2SiH + ClCH_2CH_2Cl \rightarrow PhCl_2SiCH_2CH_2Cl}$$

$$\mathrm{PhCl_2SiCH_2CH_2Cl \xrightarrow[-HCl]{} PhCl_2SiCH = CH_2}$$

and also

$$\mathrm{ClCH_2CH_2Cl \xrightarrow[-HCl]{} ClCH = CH_2}$$

$$\mathrm{PhCl_2SiH + ClCH = CH_2 \rightarrow PhCl_2SiCH = CH_2}$$

1-Trichlorosilyl-2-methyldichlorosilylethylene was prepared by a high-temperature condensation method in two stages.

$$\mathrm{Cl_3SiH + ClCH = CHCl \rightarrow Cl_3SiCH = CHCl}$$

$$\mathrm{Cl_3SiCH = CHCl + HSiCl_2CH_3 \rightarrow Cl_3SiCH = CHSiCl_2CH_3}$$

All the individual polyradicals synthesized on the basis of the organochlorosilanes enumerated above, their physical constants, yields and elemental analyses are given in Table 1.

The EPR spectra of dilute solutions of the polyradicals were taken under standard conditions in the absence of oxygen. As is evident from Fig. 1, the EPR spectra of the tetraradicals (I)-(V) (Table 1) consist of nine lines with good resolution. In Fig. 2 we give the EPR spectral data for pentaradicals (VI)-(IX) which consist of eleven significantly less resolved lines.

When the EPR spectra of the hexaradicals (X)-(XV) are considered (Fig. 3), it becomes evident that with increase in the length of the connecting bridge, the hyperfine structure of the spectra hardly changes, and is a system of thirteen weakly resolved lines. An attempt to prepare the geometric isomers

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TABLE 1. Constants and Yields of Individual Iminoxyl Polyradicals

No.	Formula	Yield, %	mp, °C	Empirical formula	Found, %			Calculated, %			Mol. wt.*		Spin/M·10²⁴		No. of lines
					C	H	N	C	H	N	found	calc.	found	calc.	
I	$R_2CH_3SiCH_2CH_2SiCH_3R_2$†	34.6	123—124	$C_{40}H_{78}O_8N_4Si_2$	60,00	9.62	6.98	60.12	9.83	7.01	799.2		2.4	2.4	9
II	$R_2C_6H_5SiCH_2CH_2SiC_6H_5R_2$	38.0	173	$C_{50}H_{82}O_8N_4Si_2$	65,30	9.00	6.28	65.05	8.95	6.06	923.3	940	2.4	2.4	9
III	$R_2C_6H_5SiCH_2CH_2SiCH_3R_2$	26.0	97—98	$C_{45}H_{80}O_8N_4Si_2$	62.50	9.36	6.31	62.69	9.87	6.55	861.3		2.4	2.4	9
IV	$R_2CH_3SiCH = CHSiCH_3R_2$	34.7	149—150	$C_{40}H_{76}O_8N_4Si_2$	59,93	9.51	7.19	60.26	9.61	7.02	797.2	800	2.3	2.4	9
V	$R_2C_6H_5SiCH = CHSiC_6H_5R_2$	45.0	165—165,5	$C_{50}H_{80}O_8N_4Si_2$	64.85	8.84	5,72	65.19	8.75	6.07	921.3		2.5	2.4	9
VI	$R_2CH_3SiCH_2CHSiR_3$	58.0	112	$C_{48}H_{92}O_{10}N_5Si_2$	60.12	9.59	7.13	60.37	9.71	7.33	955.1	980	2.8	3.0	11
VII	$R_2C_6H_5SiCH_2CH_2SiR_3$	30.0	98—99	$C_{53}H_{96}O_{10}N_5Si_2$	62.47	9.52	6.86	62.49	9.41	6.81	1019.4		3.1	3.0	11
VIII	$R_2CH_3SiCH_2CH_2CH_2SiR_3$	21.2	oil	$C_{49}H_{94}O_{10}N_5Si_2$	60,45	9.84	7.08	60.71	9.77	7.22	969.4		2.7	3.0	11
IX	$R_2CH_3SiCH = CHSiR_3$	31.8	143—146	$C_{48}H_{90}O_{10}N_5Si_2$	60.11	9.26	7.0	60.46	9.51	7.34	952.4	925	2.6	3.0	11
X	$R_3SiCH_2SiR_3$	24.0	199	$C_{55}H_{104}O_{12}N_6Si_2$	60.05	9.55	7.86	60.19	9.55	7.65	1097.5		3.4	3.6	13
XI	$R_3SiCH_2CH_2Si — R_3$	57.0	186	$C_{56}H_{106}O_{12}N_6Si_2$	60.50	9.40	7.40	60.49	9.61	7.55	1111.7	1187	3.5	3.6	13
XII	$R_3SiCH = CHSiR_3$	54.2	169—170	$C_{56}H_{106}O_{12}N_6Si_2$	60.45	9.39	7.50	60.60	9.74	7.57	1109.6		3.5	3.6	13
XIII	$R_2Si(CH_2CH_2SiCH_3R_2)_2$	28.5	oil	$C_{60}H_{118}O_{12}N_6Si_3$	60.22	9.97	6.30	60.05	9.91	6.99	1199.8	1200	3.4	3.6	1
XIV	$R_3SiCH_2CH_2CH_2SiR_3$	22.4	134—135	$C_{57}H_{110}O_{12}N_6Si_2$	60.57	9.82	7.45	60.71	9.83	7.45	1127.7		3.4	3.6	13
XV	R_3Si—  —SiR_3	61.5	188—189	$C_{60}H_{108}O_{12}N_6Si_2$	61.97	9.21	7.14	62.05	9.30	7.23	1160.8	1140	3.6	3.6	13
XVI	$R_2Si(CH_2 \equiv CH_2 - SiR_3)_2$	20.0	oil	$C_{76}H_{144}O_{16}N_8Si_3$	60.61	9.66	7.14	60.45	9.61	7.42	1410		4.3	4.8	1

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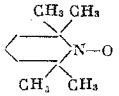
* The mol. wt. was determined by an ebullioscopic method [18].

†R = —O—


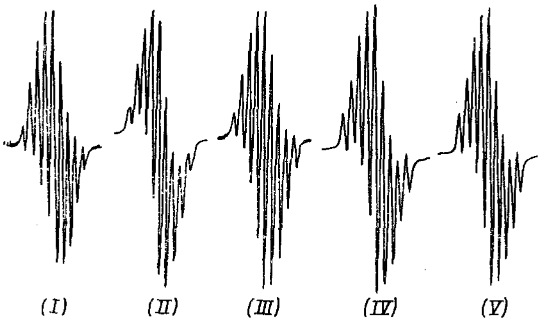


Fig. 1. Hyperfine structure of EPR spectra of dilute deoxygenated solutions of individual tetraradicals (I)-(V) in tetrahydrofuran.

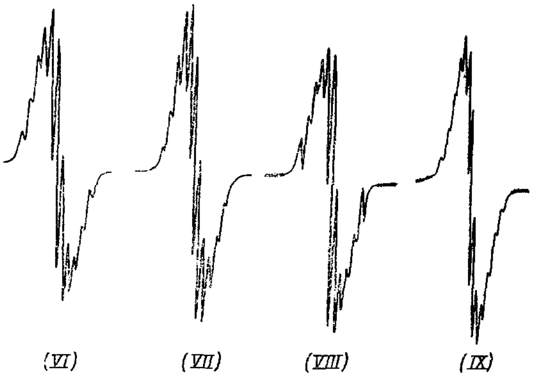


Fig. 2. Hyperfine structure of EPR spectra of pentaradicals (VI)-(IX) in tetrahydrofuran.

of polyradical (XII), based on the corresponding cis- and trans-isomers of 1,2-bis(trichlorosilyl)ethylene, was not successful, and one and the same hexaradical was obtained in each case.

Comparing the EPR spectra of the tetra-, penta- and hexaradicals, attention becomes drawn to the fact that resolution of the hyperfine spectra sharply decreases as the paramagnetic centers accumulate. We suggest that for polyradicals including more than six paramagnetic centers per single particle the EPR spectrum should be a single line.

EXPERIMENTAL

1,2-bis(Phenyldichlorosilyl)ethane. Into a three-neck round-bottom flask, provided with a stirrer, dropping funnel and reflux condenser ending in a calcium chloride tube, were charged 5.5 g of phenylvinyldichlorosilane and 0.1 ml of the Speier catalyst. To the mixture was slowly added 7.2 g of phenyldichlorosilane, after which the reaction mixture was heated at 130° for 5 h. By vacuum distillation from a Claisen flask there was obtained 5.0 g (48.5%) of a compound having bp 157-159° at 1.5 mm, n_D^{20} 1.5700. Found %: Cl 38.12. $C_{14}H_{14}Cl_4Si_2$. Calculated %: Cl 38.30.

1-Methyldichlorosilyl-2-phenyldichlorosilylethylene. To a mixture of 10.0 g of methylvinyldichlorosilane [16] and 0.4 ml of Speier catalyst was slowly added 19.0 g of phenyldichlorosilane, after which the reaction mixture was heated at 100° for 5 h. By distillation from a Claisen flask there was obtained 10.7 g (47.3%) of a compound having bp 113° at 1.5 mm, n_D^{20} 1.5264. Found %: Cl 44.30. $C_9H_{12}Cl_4Si_2$. Calculated %: Cl 44.55.

1,1,1,4,4,7,7,7-Octachlorotrisilylethylene. To a mixture of 3.8 g of divinyldichlorosilane and 0.1 ml of Speier catalyst was slowly added 10.0 g of trichlorosilane, after which the reaction mixture was boiling for 3 h. By vacuum distillation there was isolated 6.8 g (63.8%) of a compound having bp 117-118° at 2 mm; mp 56-57° (in sealed capillary). Literature [15]: bp 140-142° at 6 mm; mp 58-60°.

1,1,4,4,7,7-Hexachloro-1,7-dimethyltrisilylethylene. Analogously to the preceding experiment, 3.8 g of divinyldichlorosilane and 8.5 g of methyldichlorosilane yielded 5.7 g (60.0%) of a substance of bp 128-129° (2 mm); mp 82-83° (in a sealed capillary). Literature data [15]: bp 165-166° (13 mm), mp 80-81°.

1-Methyldichlorosilyl-2-trichlorosilylethylene. A mixture of 48.9 g of β-chlorovinyltrichlorosilane and 48.9 g of methyldichlorosilane was passed through a quartz tube (length, 50 cm; diameter, 2.8 cm) at 575° over a 2 h period. By distillation in a column, 26.0 g (37.9%) of a compound having bp 195-200° at 735.7 mm; n_D^{20} 1.4824, was isolated. Found %: Cl 64.30. $C_3H_5Cl_5Si$. Calculated %: Cl 64.59.

Phenylvinyldichlorosilane. A mixture of 178.0 g of phenyldichlorosilane and 148.5 g of dichloroethane was passed through the same tube at 575° over a 5-h period. By distillation in a column, 9.5 g (4.7%)* of a compound having bp 222-225° at 735.3 mm; n_D^{20} 1.5322, was isolated. Literature [17]: bp 121° at 36 mm, n_D^{25} 1.5335.

Iminoxyl Polyradicals. To a mixture of 0.00116 mole of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, 30 ml of absolute benzene, and 2 ml of triethylamine was added, with thorough mixing,

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* Under analogous conditions the yield of methylvinyldichlorosilane was 19.5%; according to the literature [16], it is 10%.

an equimolecular amount of the appropriate organochlorosilane in 20 ml of benzene. The reaction mixture was boiled for 5 h. The precipitate formed was filtered off and the filtrate was evaporated under vacuum. After the usual purification by crystallization or reprecipitation, analytically pure preparations were obtained (see Table 1).

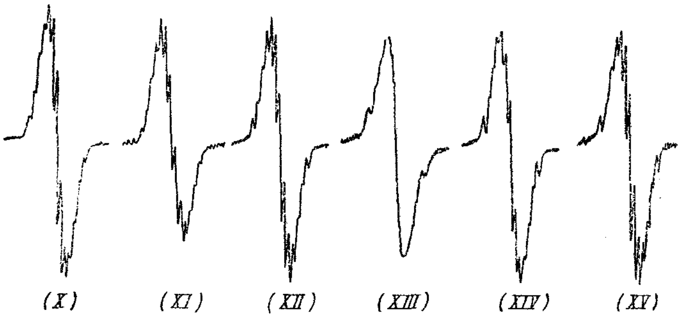

Fig. 3. Hyperfine structure of EPR spectra of hexaradicals (X)-(XV) in tetrahydrofuran.

CONCLUSIONS

1. A series of individual organosilicon tetra-, penta- and hexaradicals has been prepared for the first time.

2. The previously discovered phenomenon of electron exchange in polyradicals has a general character.

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