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ORGANO-SILANES AND -GERMANES WITH CHELATED AND/OR NON-CHELATED OXINATO LIGANDS

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Summary

Several tri- and di-organo(oxinato)-silanes and -germanes have been prepared from corresponding organo-silazanes or -germazanes The UV spectra indicate that the compounds involve either chelated or non-chelated oxinato groups or both depending on the number and kind of organic groups on the metal atom The PMR spectra of $RR'Si(Ox)_2$ (R = alkyl, R' = vinyl or phenyl) are interpreted in terms of rapid exchanges between the two kinds of oxinato groups

Introduction

Group IV organometallic compounds, organotin and organolead complexes involving penta- or hexa-coordinated metals have been extensively studied [1 - 5]. Penta- or hexa-coordinated silicon or germanium complexes are also not uncommon for inorganic and monoorganosilicon derivatives [1,3,6 - 8] However, such coordination has not well been established for compounds having two or three carbon atoms bonded to a silicon or germanium atom, some di- and triorganofluorosilicate anions [9,10] and the so-called triphenyl (bipyridine)siliconium ion [11] being notable exceptions Hexa-coordinated chelate structures occur in the inorganic derivative, $SiA_3Cl{\cdot}HCl$ (A = acetylacetonato group) and also for monoalkyl compounds of the type, $RSiA_2Cl$, but the dimethyl- and trialkylsilyl derivatives have tetra-coordinated open-chain structures [12]. Penta- or hexa-coordinate transition states have also been invoked for the racemization or tautomerization of organosilanes [13,14]. Quite recently the preparations of Schiff-base chelates of diphenylgermane were reported [15].

Previous papers from our laboratory described some studies on the oxinato complexes of organo-tins [16 - 21] and -leads [20,21]. We recently reported the preparation of organo(oxinato)silanes, $(CH_3)_3Si(Ox)$ and

$R_2Si(Ox)_2$ ($R = CH_3$, C_6H_5) by the reaction of corresponding silazane and 8-hydroxyquinoline as shown below [23]. On the basis of UV spectra we proposed that $(C_6H_5)_2Si(Ox)_2$ contains hexa-coordinated silicon while the other two compounds contain tetra-coordinated silicon. In this report we describe the preparations of analogous organo(oxinato)germanes and some mixed tri- or di-organo(oxinato)silanes. Structural information obtained from their UV and PMR spectra is also discussed.

$$R_3SiNHSiR_3 + 2\ HOx \rightarrow 2\ R_3Si(Ox) + NH_3$$

$$[R_2SiNH]_n + 2\ HOx \rightarrow R_2Si(Ox)_2 + NH_3$$

Experimental

Starting materials

8-Hydroxyquinoline was of commercial pure grade. 5-Methyl-8-hydroxyquinoline was prepared by a published method [24].

The organosilazanes shown in Table 1 were prepared by the usual method [25], viz., addition of gaseous dry ammonia to an appropriate solution of organochlorosilanes Hexamethyldigermazane [26], hexaphenyldigermazane [27], bis(diethylamino)dimethylgermane* [28], and diphenylgermazane [29]

TABLE 1

PROPERTIES AND ANALYTICAL RESULTS OF ORGANOMETALAZANES

Compound[a]	B p (°C/mm) or m p (°C)	Analysis found (calcd) (%) C	H	N
$[(CH_3)_2(C_6H_5)Si]_2NH$	137 - 145/2.5 - 4[b]	67.00 (67.30)	8.14 (8.12)	4.66 (4.91)
$[(CH_3)(C_3H_5)SiNH]_3$	113 - 114.5[c]	61.65 (62.17)	6.72 (6.71)	10.09 (10.36)
$[(CH_3)(C_6H_5)SiNH]_4$	202 - 204	62.18 (62.17)	6.81 (6.71)	10.19 (10.36)
$[(CH_3)(CH_2{=}CH)SiNH]_3$	59 - 61.5/1	41.95 (42.30)	8.56 (8.28)	15.14 (16.44)
$[(C_2H_5)(CH_2{=}CH)SiNH]_3$	120 - 122/3	48.07 (48.43)	9.07 (9.14)	13.68 (14.12)
$[(p\text{-}CH_3C_6H_4)_2SiNH]_3$	239 - 240	74.71 (74.61)	6.92 (6.71)	6.13 (6.22)
$[(CH_2{=}CH{-}CH_2)_2SiNH]_3$	153/2	57.36 (57.54)	8.93 (8.85)	10.71 (11.18)
$[(CH_2{=}CH{-}CH_2)_2SiNH]_4$	69 - 69.5	57.04 (57.54)	9.08 (8.85)	10.76 (11.18)
$[(C_6H_5CH_2)_2SiNH]_3$	87.5 - 89	74.46 (74.61)	6.61 (6.71)	6.10 (6.22)
$[(C_6H_5CH_2)_2SiNH]_4$	165 - 165.5	74.62 (74.61)	6.80 (6.71)	6.12 (6.22)
$[(C_6H_5)_3Ge]_2NH$	153 - 159[d]	69.34 (69.42)	5.17 (5.02)	2.00 (2.25)

[a] The degree of polymerization of the cyclosilazanes were determined from the mass spectra recorded on a Hitachi RMU-6E spectrometer at 70 eV [b] Reported b p 128 - 129°/2 - 3 mmHg [24] [c] Reported m.p 115 - 116° [24]. [d] Reported m p 156 - 157° [26]

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* The reaction of $(CH_3)_2GeCl_2$ with ammonia gives a mixture of $[Cl(CH_3)_2Ge]_3N$ and polymeric compound of the composition, $(CH_3)_2GeN_{2/3}$ [30], which was considered to be an unsuitable starting material for the reaction with 8-hydroxyquinoline

were prepared by published methods or by the method analogous to that mentioned above for organosilazanes In the reactions with 8-hydroxyquinoline, diorganosilazanes of type [RR'SiNH]$_n$ were used without rigorous separation of the oligomeric isomers.

Preparation of organo(oxinato)-silanes and -germanes

Essentially the same procedures were used to prepare the organo(oxinato)-silanes and -germanes needed for this work as were described previously [23]. Dry toluene was used as the solvent except for the reaction of diphenyltetramethyldisilazane, which was heated at 150 - 160° for one h without solvent. The yields after repeated crystallization or distillation of the products were in the 30 - 50% range

Diallylsilazane and dibenzylsilazane reacted with 8-hydroxyquinoline to evolve ammonia, but the corresponding diorgano(oxinato)silanes could not be isolated. The PMR spectra of their reaction mixture showed the absence of methylene protons attached to silicon atom. Hexaphenyldigermazane also reacted with 8-hydroxyquinoline, but hexaphenyldigermoxane was always isolated as the main product.

The physical properties and analytical data for organo(oxinato)-silanes and -germanes prepared are given in Table 2

Physical measurements

The UV spectra of solution were measured on a Hitachi 124 Spectrophotometer. Since organo(oxinato)silanes and -germanes are sensitive to moisture in dilute solution, the spectra of these compounds were also recorded with the Nujol mulls by the literature method [31] using an Hitachi Two-Wavelength Double Beem Spectrophotometer model 356. The results are summarized in Table 3, in which solution spectral data are shown for those com-

TABLE 2

PROPERTIES AND ANALYTICAL RESULTS FOR ORGANO(OXINATO)SILANES AND -GERMANES

Compound	Color^{a}	B p (°C/mm) or m p (°C)	Analysis, found (calcd) (%) C	H	N
(III) $(CH_3)_2(C_6H_5)Si(Ox)$	C	166 5 - 168 5/3	72 97	5 88	5 21
			(73 08)	(6 13)	(5 01)
(IV) $(CH_3)(C_6H_5)Si(Ox)_2$	Y	169 - 170	73 62	5 01	6 78^{d}
			(73 50)	(4 93)	(6 86)
(V) $(CH_3)(CH_2{=}CH)Si(Ox)_2$	Y	110 - 112	70 36	4 96	8 04
			(70 36)	(5 06)	(7 82)
(VI) $(C_2H_5)(CH_2{=}CH)Si(Ox)_2$	Y	101 - 105	71 20	5 46	7 37
			(70 94)	(5 41)	(7 52)
(VII) $(C_2H_5)(CH_2{=}CH)Si(Ox\text{-}5\text{-}CH_3)_2$ ^{b}	Y	133 - 138	71 98	6 03	7 28
			(71 97)	(6 04)	(6 99)
(IX) $(p\text{-}CH_3C_6H_4)_2Si(Ox)_2$	Y	260 5 - 262 5	77 20	5 43	5 42^{e}
			(76 77)	(5 64)	(5 60)
(X) $(CH_3)_3Ge(Ox)$	C	120 - 121/4	55 24	5.71	5 54
			(55 05)	(5 77)	(5 35)
(XI) $(CH_3)_2Ge(Ox)_2$	C	187 - 189	61 06	4 58	7 12
			(61 44)	(4 64)	(7 16)
(XII) $(C_6H_5)_2Ge(Ox)_2$	Y	270 - 272^{c}	70 05	4 36	5 46
			(69 95)	(4 31)	(5 44)

^{a}Y yellow, C colourless or white ^{b}5-Methyloxinato ^{c}Reported 140° decomp [32] ^{d}% Si 6 77(6 87) ^{e}% Si 5 61(5 60)

TABLE 3
UV AND PMR DATA OF ORGANO(OXINATO) SILANES AND GERMANES

Compound		UV spectra			PMR Spectra[c]			
		Solvent	λ_{max}[b] (nm)		2 H	3 H	4-H	M-R[d]
	H—Ox	CH_2Cl_2	315 (2 38)		8 69	7 37	8 11	
	H—Ox 5 CH_3	CH_2Cl_2	330 (2 80)		8 65	7 34	8 15	
(I)	$(CH_3)_3Si(Ox)$[a]	CH_2Cl_2	306 (3 54)		8 66	7.19	7 92	0 36
(II)	$(CH_3)_2(C_6H_5)Si(Ox)$	CH_2Cl_2	307 (3 70)		Not measured			
(III)	$(CH_3)_2Si(Ox)_2$[a]	Nujol	308		8 74	7 39	8 11	0 57
(IV)	$(CH_3)(C_6H_5)Si(Ox)_2$	CH_2Cl_2	307 (5 06)	369 (3 29)	8 52	[e]	8 01	0 41
		Nujol	310	368				
(V)	$(CH_3)(CH_2{=}CH)Si(Ox)_2$	Nujol	312	380	8 77	7 38	8 17	0 54
(VI)	$(C_2H_5)(CH_2{=}CH)Si(Ox)_2$	CH_2Cl_2	307 (4 99)	366 (2 21)	Not measured			
		Nujol	307	366				
(VII)	$(C_2H_5)(CH_2{=}CH)Si$-$(Ox$-$5\ CH_3)_2$	Nujol	300	390	8 54[f]	7 21[g]	8 12[h]	0 89[i]
(VIII)	$(C_6H_5)_2Si(Ox)_2$[a]	CH_2Cl_2		368 (5.64)	Not measured			
(IX)	$(p\text{-}CH_3C_6H_4)_2Si(Ox)_2$	CH_2Cl_2		368 (4 99)	Not measured			
(X)	$(CH_3)_3Ge(Ox)$	Nujol	320		8 68	7 27	8 00	0 58
(XI)	$(CH_3)_2Ge(Ox)_2$	Nujol	320		8 75	7 29	8 22	0 96
(XII)	$(C_6H_5)_2Ge(Ox)_2$	Nujol		377	8 55	[e]	8 00	

[a] Reported previously [23] [b] Extinction coefficients ε (M^{-1} cm^2) × 10^{-3} are shown in parentheses [c] Measured at 23° in CH_2Cl_2 except for compound (V) in $CDCl_3$ [d] CH_3 or C_2H_5 proton signals [e] Could not be resolved due to the presence of phenyl ring proton signals [f] 8 46 at −30°, 8 33 at −60° [g] 7 14 at −30°, 7 14 at −60° [h] 8 07 at −30°, 8 03 at −60° [i] 0 78 at −30°, 0 66 at −60°

pounds which gave the same spectra in solution and in the solid state The PMR spectra were measured on a JEOL model JNM-3H-60 and a JNM-PS-100 spectrometer, operating at 60 and 100 MHz, respectively. The concentration was 5 to 6% w/w. Chemical shifts shown in Table 3, were measured relative to TMS as internal standard The assignments shown in Table 3 were performed in the same procedure as used for other organometal oxinates [21].

Results and discussion

Preparation

Organo-tin and -lead oxinates were prepared by the reaction of corresponding organometal halide and 8-hydroxyquinoline in an alkaline protic solution [16,17,22]. Huber and Kaiser applied this method to the preparation of diphenyldi(oxinato)germane [32], but the elemental analyses of the product were satisfactory only for nitrogen, and the product was thermally unstable above 140°. The compound prepared from diphenylgermazane gave good elemental analyses, and was of superior thermal stability (Table 2). Halides were also found to be less satisfactory starting materials in the preparation of organo(oxinato)silanes [23], probably because of the difficulty of removing traces of hydrochloric acid, which acts as a catalyst for the hydrolysis or thermal decomposition of the products

UV spectra and structures

For the UV spectra of organo-tin and -lead oxinates it is known that the characteristic band (L_a band) at ca. 320 nm of 8-hydroxyquinoline shifts to longer wave-length, viz. 360 to 410 nm on chelation to tin or lead atom [17 - 20,33,34]. On this criterion, the UV spectral data for organo(oxinato) silanes shown in Table 3 indicate that triorgano- and dimethyl(oxinato)silanes, (I) - (III), are not chelated, that the mixed diorgano compounds, (IV) - (VII), contain both chelated and non-chelated oxinato groups, and that the diaryl compounds, (VIII) and (IX), have two chelated oxinato groups Thus the coordination number of these oxinatosilanes would be four for the first group of oxinatosilanes, five for the second, and six for the last group.

With the organo(oxinato)germanes, (X) - (XII), the characteristic band is observed at wave-lengths close to those of the corresponding organo(oxinato)-silanes. This indicates that both trimethyl(oxinato)germane, (X), and dimethyldi(oxinato)germane, (XI), are non-chelated, with a coordination number of four, and diphenyldi(oxinato)germane, (XII), is chelated, with a coordination number of six

The above results suggest that the number and kind of organic groups on the silicon or germanium atom play an important role in complex formation. It may be possible to interpret the results in terms of the electron-donating and -attracting properties of the organic groups, or Taft's σ^* values. Similar influence of organic groups on coordination has not been observed for organotin oxinates, all of which have been reported to have a chelate structure.

PMR spectra

Klanberg and Muettertics observed in the ^{19}F NMR spectra of $(C_6H_5)_2$-

SiF_3^- two line signals which are consistent with a penta-coordinate species of trigonal bipyramidal geometry, having two phenyl groups in equatorial positions [10]. We also expected for the PMR spectra of the mixed diorganodi(oxinato)silanes, $RR'Si(Ox)_2$, the appearance of two kinds of proton signals due to the chelated and the non-chelated oxinato ligands. The features in the oxinato 2- and 4-proton signal region, δ 9 to 8, for all the oxinatosilanes and -germanes were analogous to those of 8-hydroxyquinolines or organtin and -lead oxinates [21] which contain only one kind of oxinato ligands. In the δ 8 to 7 region the multiplets due to the oxinato 3-, 5-, 6- and 7-protons are more complicated for the compounds with silicon - phenyl bonds. Accordingly low temperature PMR spectra were measured for the compound (VII), but no appreciable signal splitting was observed between +23° and −60°, the limit of solubility, although considerable up-field shifts were observed for the 2-oxinato and Si-ethyl protons. This spectroscopic equivalence of the two oxinato ligands in $RR'Si(Ox)_2$ can be explained by postulating that the chelated and non-chelated oxinato groups are rapidly exchanging, probably intramolecularly, even at −60°, so that the PMR data shown in Table 3 are arithmetic means for both types of oxinato ligands. Analogous spectroscopic equivalence of ligands has been found for the ^{19}F NMR spectra of the system, $RSiF_5^- + F^-$, at low temperatures [10]. As for the up-field shifts of 2-oxinato and Si-ethyl protons of (VII) at lower temperatures, it seems probable that these shifts are the result of anisotropic shielding by the non-chelating oxinato ligand, which has less rotational freedom.

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