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ATRANES. I. A NEW METHOD FOR SYNTHESIZING 1-ALKYL AND ARYL SILATRANES

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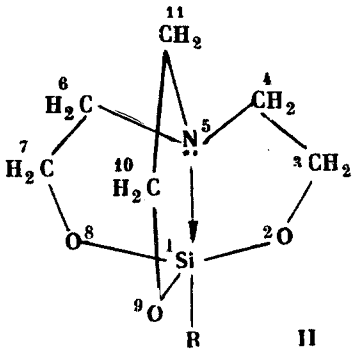
A new simple method for synthesizing organyl(2, 2', 2"-aminotriethoxy)silanes $RSi(OCH_2CH_2)_3N$, named 1-organylsilatranes, is developed. It is based on splitting polyorganylsesquisiloxanes $(RSiO_{1.5})_x$, polyorganylsiloxanols $[RSiO_{1.5-y}(OH)_{2y}]_x$, or polyorganylhydrosiloxanes $(RSiHO)_m$ with triethanolamine in the presence of an alkaline catalyst. Six compounds of the type mentioned were synthesized by this method, of which three (1-ethyl-, 1-isopropyl- and 3, 7-dimethyl-1-phenylsilatrane) were previously unknown, and certain of their properties are described. The resistance of 1-organylsilatranes to hydrolysis, their high dipole moments, and their inability to give ammonium compounds when treated with CH_3I indicate that they contain an intramolecular coordinated link Si←N. 1-Arylsilatranes have a well-defined physiological activity.

Internally complex, cyclic, complete inorganic ethers and alkoxides of triethanolamine and its derivatives, of the type $R_{n-3}M(OCH_2CH_2)_3N$ (I) [where M is an electron-accepting atom with valence 3 or higher, with an incomplete p or d shell (B^{1-15}, $Al^{16,17}$, $Si^{18,19}$, Bi^{20}, Fe^{21-24}, etc.), n is the valence, and R an organic radical, hydrogen, or other substituent] have recently begun to attract attention because of their possible practical applications and their peculiar structure and properties. It is proposed to group all compounds of type I, extensively investigated in this laboratory, under the general name of atranes: 2, 2', 2"-aminotriethoxysilane* (M = Si, R = H) or silatrane; 2', 2"-aminotriethoxyborane (M = B) or boratrane; 2, 2', 2"-aminotriethoxyaluminum (M = Al) or alumatrane; 2, 2', 2"-aminotriethoxybismuth (M = Bi) or bismatrane, and 2, 2', 2"-aminotriethoxyiron (M = Fe) or ferratrane, etc.

This paper describes a new method of synthesizing 1-organylsilatranes II and some of their properties. Compounds of type II have not previously been described in the literature.



II

Brief references to them first appeared only a few years ago in a patent [18], and in a letter to the editor, but no experimental data were given. In every case synthesis of such compounds is effected by transetherification of the corresponding triethoxysilanes with triethanolamine according to the equation:

$$RSi(OC_2H_5)_3 + (HOCH_2CH_2)_3N \rightarrow RSi(OCH_2CH_2)_3N + 3C_2H_5OH,$$

R = alkyl, alkenyl, aryl, or alkoxyl.

The comparatively high stability of the compounds thus prepared, and the slowness with which they are neutralized with hydrochloric acid, led, by analogy with the corresponding boron compound, to the conclusion that they contained an intramolecular coordination link between the nitrogen and silicon atoms [19]. The lowering of the frequency of the Si – H valence vibration (from 2196 cm^{-1} in $HSi(OCH_2CH_3)_3$ to 2137 cm^{-1} in II, R = H) was also taken as evidence of the existence of the intramolecular complex linkage Si←N.

A simple and convenient method of synthesizing 1-organylsilatranes [25] has been worked out, using starting materials which are more accessible than the corresponding organyltriethoxysilanes. It is based on the splitting of hydrolysis products of organyltrichlorsilanes, i. e., polyorganylsesquisiloxanes $(RSiO_{1.5})_x$ or polyorganylsiloxanols

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*Or 2, 2', 2" -nitrilotriethoxysilane

$[\mathrm{RSiO_{1.5-y}(OH)_{2y}}]_x$ ($y = 0-1.5$), by triethanolamine in the presence of catalytic quantities of alkali metal hydroxides (preferably KOH) according to the equation*:

$$1/x[\mathrm{RSiO_{1.5-y}(OH)_{2y}}]_x+\mathrm{(HOCH_2CH_2)_3N}\rightarrow \mathrm{R}\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}+$$
$$+(1.5+y)\mathrm{H_2O}.$$

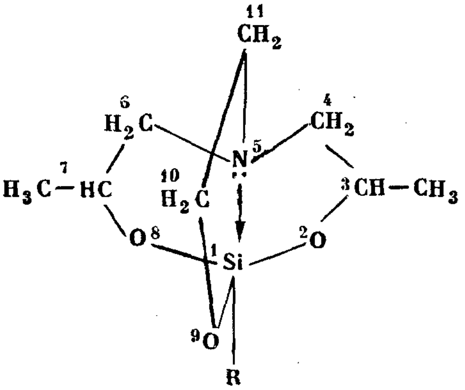
The resultant water is removed from the reaction mixture by continuous azeotropic distillation, using a suitable inert solvent (xylene). Progress and completion of the process can readily be followed from the volume of water liberated. The reaction rate increases as the degree of condensation of initial siloxanols falls. Vinyl and phenyl derivatives react considerably faster with triethanolamine than do alkyl derivates. 1-Organylsilatranes are precipitated in a crystalline state when the reaction mixture is cooled, and are purified by recrystallization.

Polyorganylhydrosiloxanes of the type $(\mathrm{RSiHO})_m$, prepared by hydrolysis of the corresponding organyldichlorosilanes, can, like the products of hydrolysis of organyltrichlorosilanes, be used as starting materials for synthesis of 1-organylsilatranes. The reaction takes place under the same conditions, the equation being

$$1/m(\mathrm{RSiHO})_m+\mathrm{N(CH_2CH_2OH)_3}\rightarrow \mathrm{R}\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}+\mathrm{H_2O}+\mathrm{H_2}.$$

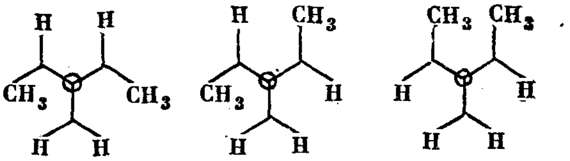
When triethanolamine reacts with polyorganylhydrosiloxanes, the Si–H bond first undergoes reaction, hydrogen being evolved (the theoretical amount of hydrogen is evolved long before the end of the reaction), and only then do the siloxane bonds undergo fission with formation of water. Hence the end of the reaction is not indicated by hydrogen evolution ceasing, but by cessation of water formation.

The table gives the yields, by both methods, of the 6 organylsilatranes (three being previously unknown), their melting points, solubilities in water, analytical data, and experimentally determined molecular weights. Also included among these compounds is 3,7-dimethyl-1-phenylsilatrane (III), obtained by reacting polyphenylsesquisiloxane with diisopropanolethanolamine.



III

All the compounds synthesized are colorless solids, crystallizing in large beautiful crystals of various forms and having sharp melting points. The sole exception is 3,7-dimethyl-1-phenylsilatrane, which is a wax-like substance.** It melts over a rather wide range (86.5-89°) and may be a mixture of three possible stereoisomeric forms



It was found possible to separate two of them, as needle-shaped crystals m.p. 90.4-91.4°, and as plates m.p. 94.8-95.8°.

1-Methylsilatrane is polymorphous and has two melting points. After crystallizing from xylene it melts at 142-143°, but, after rapid cooling of the melt, at 151.5-152.5°. Sometimes when it is recrystallized from heptane or or xylene the more stable, high-melting form, m.p. 151.5-152.5°, is formed; this is unchanged by repeated cooling and heating of the melt. These data are in agreement with those in the literature [19], which state that when 1-methylsilatrane is crystallized from the melt, a low-melting form, m.p. 123-125°, is formed.

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*One of the authors previously showed that siloxanes can be catalytically split by alcohols to give the corresponding alkoxysilanes [26].

**Similarly many C-substituted boratranes are also wax-like [15].

All the 1-organylsilatranes synthesized are quite thermostable, and sublimate unchanged in a vacuum or even at ordinary pressure. They behave as if they were monomolecular, and the view that they are finds conclusive confirmation in the results of cryoscopic molecular weight determinations in nitrobenzene (see table) and benzene. They are quite soluble in halogenated hydrocarbons, nitrobenzene, dimethylformamide, and acetonitrile. Methyl and ethyl derivatives are quite soluble in water. The nature of the hydrocarbon radical attached to the silicon atom has an important effect on the solubilities of 1-organylsilatranes in organic solvents. For example, 1-methylsilatrane is practically insoluble in diethyl ether. At the same time, its nearest homologs, 1-ethyl- and 1-isopropylsilatrane are quite soluble in ether. The solubility of 1-ethylsilatrane in xylene is less than that of the isopropyl compound, but solubility in water is higher than that of the latter. As a rule 1-arylsilatranes are less soluble in the majority of solvents than are the 1-alkylsilatranes.

Unlike the readily hydrolyzable organyltriethoxysilanes, the 1-organylsilatranes are rather stable with respect to atmospheric moisture (and oxygen). Appreciable hydrolytic fission of 1-methylsilatrane is observed only after it has been in an open vessel in air with 50% relative humidity for 28 days. 1-Isopropylsilatrane and 1-phenylsilatrane are unchanged after over 1 1/2 years storage under similar conditions. Such stability can be explained only by the existence of an intramolecular coordination link between the nitrogen and silicon atoms. The high values of the dipole moments of 1-organylsilatranes (5-7 D)*, as well as the absence of appreciable well-defined donor properties in the nitrogen atom (1-organylsilatranes do not give ammonium derivatives with methyl iodide) conclusively demonstrate the presence of such a link.

A characteristic property of 1-organylsilatranes (and in particular of 1-isopropylsilatrane) is their capacity for undergoing intensive contact motion when crystalline particles are placed on the surface of a liquid (water, benzene, etc.).

1-Arylsilatranes are characterized by a clearly marked physiological activity. In particular, 1-phenylsilatrane is quite highly toxic towards warm-blooded animals (twice the toxicity of strychnine), while in sublethal doses (for white mice LD_{50} = 0.4 mg/kg) it causes intense motor excitation phenomena and respiratory effects [27].

EXPERIMENTAL

Starting materials. The triethanolamine used was a pure commercial grade, which was then twice vacuum-distilled. The polyorganylsesquisiloxanes (polyorganylsiloxanols) were prepared by adding the corresponding organotrichlorosilanes, purified by distilling through a column, to a large excess of distilled water. The precipitate formed was washed with a large amount of water (to a negative reaction for Cl^-), filtered off with suction, and dried at room temperature in a

Organylsilatranes $RSi(OCH_2CH_2)_3N$

R	Compound	M. p., °C	Solubility in water g/100 g solution	Neutralization equivalent		(Cryoscopic in nitrobenzene)		Empirical formula	Found, %			Calculated, %			Yield of anide substance %
				Found	Calculated	Found	Calculated		Si	C	H	Si	C	H	
CH_3	1-Methylsilatrane	142—143 151.5—152.5	17.0	190	189	187 187	189	$C_7H_{15}NO_3Si$	14.63 14.87	44.65	7.89	14.83	44.42	7.99	90 80***
C_2H_5*	1-Ethylsilatrane	132—133.5	20.0	204	203	197 203	203	$C_8H_{17}NO_3Si$	13.82 13.71	47.73	8.51	13.81	47.26	8.43	83 93***
$(CH_3)_2CH$*	1-Isopropylsilatrane	106.5—107.5	4.5	218	217	210 212** 212 222	217	$C_9H_{19}NO_3Si$	12.60 12.66	49.87	8.76	12.92	49.74	8.81	87
$CH_2{=}CH$	1-Vinylsilatrane	165—166.2	8.4	203	201	202 205	201	$C_8H_{15}NO_3Si$	13.98 14.06	47.85	7.47	13.94	47.73	7.51	92
C_6H_5	1-Phenylsilatrane	210.3—211.3	0.5	253	251	242 244	251	$C_{12}H_{17}NO_3Si$	11.15 11.19	57.05	6.66	11.17	57.34	6.82	83
III*	3,7-Dimethyl-1-phenylsilatrane	86.5—89	0.7	280	279	273 275	279	$C_{14}H_{21}NO_3Si$	10.15 10.33	60.66	7.66	10.05	60.18	7.58	80

*New Compound. **In benzene. ***From $(RSiHO)_m$.

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*Detailed data relating to dipole moments, IR spectra, PMR spectra, and the structure of 1-organylsilatranes will be given in subsequent papers.

current of dry air. Sometimes it was dried to constant weight over conc. H_2SO_4. Polyorganylhydrosiloxanes were prepared by hydrolysis of the corresponding organyldichlorosilanes in the way previously described [28]. Diisopropanolethanolamine was prepared by condensing propylene oxide with ethanolamine in aqueous solution, b.p. 167-170° (4 mm), n_D^{20} 1.4712.

All syntheses were carried out in apparatus with ground glass joints, comprising a round bottomed flask, equipped with a mechanical stirrer having a gastight seal, and a reflux condenser, connected across a trap for separating water. When polyorganylhydrosiloxane was the starting material, the reflux condenser was also connected to a graduated gasholder for collecting the hydrogen evolved. 0.11 mole of the appropriate polyorganylsesquisiloxane (polyorganylsiloxanol) or polyorganylhydrosiloxane, 0.10 mole triethanolamine, 0.1 g powdered KOH, and 100 ml anhydrous xylene were placed in the reaction flask. The mixture was stirred and heated to vigorous boiling, this being continued until water ceased to separate in the trap, which required 1-8 hrs. The resultant solution was filtered hot and slowly cooled. The crystals of 1-organylsilatrane which separate were filtered off with suction, washed with petroleum ether, and vacuum-dried at room temperature. The compounds in which R = CH_3, $CH_2{=}CH$, and C_6H_5 were purified by recrystallizing from xylene, those where R = $(CH_3)_2CH$ by recrystallizing from petroleum ether, while for the rest n-heptane was used. In isolating 1-ethyl- and 1-isoprophylsilatrane, most of the solvent was first distilled off.

Analysis. The neutralization equivalent was determined by titrating in water with 0.1 N HCl, using methyl orange as an indicator, until a red color appeared and did not vanish when the solution was heated. Carbon and hydrogen were determined on one sample by combustion in a stream of oxygen in the presence of chromium oxide. Silicon was estimated as SiO_2, the weighed sample being "mineralized" with a mixture of oleum and conc. HNO_3, this being followed by calcination at 1000°.

Two typical syntheses are described below, by way of example.

1-Methylsilatrane. 7.38 g (0.11 mole) polymethylsesquisiloxane, 14.92 g (0.10 mole) triethanolamine, 0.1 g KOH, and 100 ml xylene were boiled together vigorously for 4 hrs, when 2.4 ml (89%) water separated. The solution was filtered hot and allowed to cool slowly to room temperature. Crystals which precipitated were filtered off with suction, washed with cold petrol ether, and vacuum-dried. Yield 15.46 g crystals m.p. 137-138°. A further 1.5 g of substance were obtained from the mother liquors. Total yield of 1-methylsilatrane 16.96 g (90%). After a few recrystallizations from xylene, or vacuum-subliming and then recrystallizing, it melts at 142-143°. After cooling the melt, the substance again melts at 151.5-152.5°.

1-Ethylsilatrane. A mixture of 7.42 g (0.1 mole) polyethylhydrosiloxane, 14.92 (0.1 mole) triethanolamine, 0.1 g KOH, and 50-100 ml xylene was slowly heated to boiling. Right at the commencement of boiling there was vigorous evolution of hydrogen, but this ceased after 1 hr 15 min, the total volume formed being 2.2 *l* (98%). On further vigorous boiling of the reaction mixture, the theoretical amount of water (1.8 ml) separated after 1 hr 45 min. The xylene solution was filtered hot, and most of the solvent distilled off from the filtrate. When the walls of the vessel were rubbed with a glass rod, crystals of 1-ethylsilatrane came down from solution. They were removed on a suction filter, washed with cold petroleum ether, and vacuum-dried. Yield 16.9g. Another 1.9 g or substance could be obtained from the mother liquors. Total yield 1-ethylsilatrane m.p. 129-130.5°, 18.8 g (93%). After crystallizing from heptane m.p. 132-135°.

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