

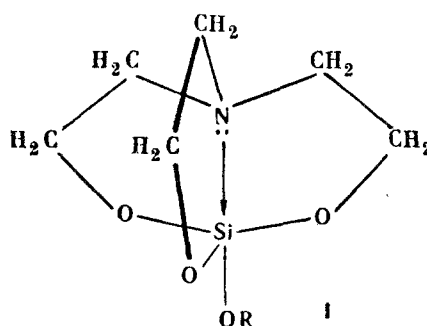
## ATRANES. IV\*. 1-ALKOXYASILATRANES

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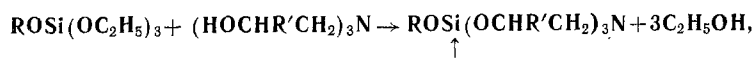
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A new method of synthesizing 1-alkoxysilatranes  $\text{ROSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$ , is described. It is based on transesterification of lower tetraalkoxysilanes with an equimolar mixture of triethanolamine and appropriate alcohol. The method is used to prepare 15 compounds of this type in 50-90% yields. Of these only one,  $\text{R} = \text{C}_2\text{H}_5$ , was previously known. Their solubilities in various solvents are found. Molecular weight determinations show them to be monomeric.

Previous papers [1-4] have described a new method of synthesizing 1-organylsilatranes (organyl[2, 2', 2''-aminotriethoxy]silanes)  $\text{RSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$  and many of their interesting properties. The present paper describes a new method of preparation and some of the properties of 1-alkoxysilatranes (I). Previously, only three compounds of this type were known: 1-ethoxy- [5-7]; 3, 7, 10-trimethyl-1-ethoxy- [7], and 1-menthoxy-silatranes [6]. They were all made by the



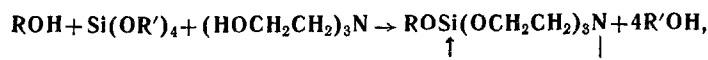
transesterification of tetraethoxysilane or menthoxytriethoxysilane with triethanolamine or triisopropanolamine according to the equation



where  $\text{R} = \text{ethyl, 1-menthyl}$ ;  $\text{R}' = \text{H, CH}_3$ .

This is not a satisfactory general method for obtaining 1-organosilatranes because of the necessity of preparing the corresponding starting alkoxytriethoxysilanes.

The new general method that has been developed for preparing 1-organosilatranes [8] is based on the transesterification of lower tetraalkoxysilanes  $\text{Si}(\text{OR}')_4$  ( $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$ ), by a mixture of equimolecular amounts of triethanolamine and the corresponding alcohol ( $\text{ROH}$ ). The reaction is preferably carried out in the presence of an alkaline catalyst (alkali metal hydroxide), which speeds it up considerably and increases the yield. Some alkoxy-silatranes (I,  $\text{R} = (\text{CH}_3)_2\text{CH}, (\text{CH}_3)_3\text{C}$ , etc.) are not generally formed unless an alkaline catalyst is used. The general equation for the reaction is:



where  $\text{R} = \text{alkyl, cycloalkyl, aralkyl}$ ,  $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5$

Synthesis is effected by heating equimolecular amounts of tetraethoxysilane (or tetramethoxysilane), triethanolamine, and a solution of catalyst in the appropriate alcohol in an inert solvent (e. g., xylene), until the ethanol or methanol formed in the reaction has completely distilled off. Reaction takes 0.5-1.5 hr. The 1-alkoxysilatranes crystallize directly from the reaction products or are separated from them after distilling off the solvent and purified by recrystallization.

The table gives the 1-alkoxysilatranes prepared by this method, their melting points, analytical data, molecular weights found experimentally, and yields.

\* For Part III see [3].

1-Alkoxysilatrane  $\text{ROSi}(\text{OCH}_2\text{CH}_2)_3\text{N}$

R	Compound	Mp, °C	M		Mol. formula	Found, %			Calc., %			Neutralization equiv.		Yield of pure material, %
			Found (cryoscopically in nitrobenzene)	Calc.		Si	C	H	Si	C	H	Found	Calc.	
$\text{CH}_3$	1-methoxysilatrane	155—156	206; 210	205.29	$\text{C}_7\text{H}_{15}\text{NO}_4\text{Si}$	13.97	41.03	7.29	13.68	40.96	7.37	203	205	89; 65*
$\text{CH}_3\text{CH}_2$	1-ethoxysilatrane	102—103	220; 224	219.31	$\text{C}_8\text{H}_{17}\text{NO}_4\text{Si}$	13.45	43.76	7.57	12.81	43.81	7.81	224	219	91; 26*
$\text{CH}_3\text{CH}_2\text{CH}_2$	1-n-propoxysilatrane	79—80			$\text{C}_9\text{H}_{19}\text{NO}_4\text{Si}$	12.75	45.87	8.03	12.04	46.33	8.21	231	233	52
$(\text{CH}_3)_2\text{CH}$	1-isopropoxysilatrane	129.5—131	222; 246	233.34	$\text{C}_9\text{H}_{19}\text{NO}_4\text{Si}$	12.20	45.80	8.20	12.04	46.33	8.21	229	233	57
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2$	1-n-butoxysilatrane	113—113.5			$\text{C}_{10}\text{H}_{21}\text{NO}_4\text{Si}$	11.98	49.06	8.71	11.35	48.56	8.56	249	247	71
$(\text{CH}_3)_2\text{CHCH}_2$	1-isobutoxysilatrane	99—100			$\text{C}_{10}\text{H}_{21}\text{NO}_4\text{Si}$	11.51	48.26	8.46	11.35	48.56	8.56	250	247	62
$\text{CH}_3\text{CH}_2(\text{CH}_2)\text{CH}$	1-sec.-butoxysilatrane	131—132			$\text{C}_{10}\text{H}_{21}\text{NO}_4\text{Si}$	11.55	48.11	8.42	11.35	48.56	8.56	245	247	59
$(\text{CH}_3)_3\text{C}$	1-tert.-butoxysilatrane	146.5—147.5	251; 247	247.37	$\text{C}_{10}\text{H}_{21}\text{NO}_4\text{Si}$	11.55	48.45	8.71	11.35	48.56	8.56	248	247	66
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2$	1-n-amoxysilatrane	102.5—103.5			$\text{C}_{11}\text{H}_{23}\text{NO}_4\text{Si}$	11.15	50.66	8.73	10.47	50.55	8.87	265	261	63
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2$	1-isoamoxysilatrane	134.5—136			$\text{C}_{11}\text{H}_{23}\text{NO}_4\text{Si}$	10.70	50.94	9.00	10.47	50.55	8.87	264	261	69
$(\text{CH}_3)_3\text{CCCH}_2$	1-neopentoxysilatrane	178—180			$\text{C}_{11}\text{H}_{23}\text{NO}_4\text{Si}$	10.63	50.03	8.77	10.47	50.55	8.87	261	261	87
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2$	1-n-hexoxysilatrane	82—83	392; 386	387.64	$\text{C}_{12}\text{H}_{25}\text{NO}_4\text{Si}$	9.95	52.64	9.19	10.20	52.33	9.15	276	275	51
$\text{CH}_3(\text{CH}_2)_5\text{CH}_2$	1-n-tetradecoxysilatrane	80—81			$\text{C}_{20}\text{H}_{41}\text{NO}_4\text{Si}$	10.34	62.19	10.70	7.24	61.97	10.66	388	388	58; 32*
$\text{C}_6\text{H}_{11}$	1-cyclohexoxysilatrane	193.5—195.5	271; 273	273.41	$\text{C}_{12}\text{H}_{25}\text{NO}_4\text{Si}$	7.39	52.10	8.36	10.27	52.72	8.48	277	273	86
$\text{C}_6\text{H}_5\text{CH}_2$	1-benzylloxysilatrane	190.5—192	277; 281	281.38	$\text{C}_{13}\text{H}_{19}\text{NO}_4\text{Si}$	7.24	54.86	7.08	9.98	55.49	6.81	285	281	79

\* In absence of catalyst.

\*\* Literature data [6], melts at 100–102°, boils at 180° (0.6 mm).

All the compounds synthesized are colorless solids, which crystallize from n-heptane as fine, mainly plate-shaped crystals. 1-Alkoxysilatrane are very soluble in water and most organic solvents, e. g., chloroform, dioxane, acetone, ethyl acetate, alcohols, benzene, toluene, xylene, diethyl ether, carbon tetrachloride, but insoluble in cold petrol ether. Unlike the rest, 1-n-tetradecoxysilatrane is insoluble in water but soluble in cold petrol ether, and 1-methoxysilatrane is slightly soluble in cold benzene, toluene, xylene, and insoluble in diethyl ether and  $\text{CCl}_4$ .

The compounds synthesized are hydrolyzed faster than 1-organylsilatrane. They gradually decompose in air. With an average relative humidity of 40%, 1-methoxy-, 1-isopropoxy- and 1-tert. -butoxysilatrane do not remain unchanged for more than 6 days, while with the others there are signs of decomposition after a fortnight.

The cryoscopic molecular weights of 1-alkoxysilatrane in nitrobenzene show that they are monomeric. The structure I assigned to the alkoxysilatrane is supported by dipole moments ( $\mu = 6.29 \text{ D}$  [2] or 1-ethoxysilatrane), and by ir and PMR spectra, details of which will be published later.

Finally, it should be mentioned that 1-alkoxysilatrane can be successfully used as crystalline derivatives for identifying alcohols (and phenols).

## EXPERIMENTAL

Starting reactants. Tetraethoxysilane was obtained by twice distilling industrial-grade material over sodium. Tetramethoxysilane was made by reacting silicon tetrachloride with absolute methanol using a previously described procedure [9]; mp 117-119°,  $n_D^{20}$  1.3683. Pure grade triethanolamine was twice vacuum-distilled. All alcohols were dried over calcium metal or calcium hydride, and purified by distillation.

Analysis. Carbon and hydrogen were determined on the same sample of material by combustion without a catalyst, using chromium oxide. Silicon was determined as  $\text{SiO}_2$  by mineralizing a weighed portion of the substance with mixed strong sulfuric and nitric acids, followed by heating at 1000°.

Method of synthesis. All syntheses were effected in apparatus with ground-glass joints, comprising a round-bottomed flask fitted with a 22-cm rod and disc column, the latter equipped with a thermometer and condenser. In the flask was placed a mixture of 0.05 mole tetraethoxy or tetramethoxysilane, 0.05 mole triethanolamine, 0.1 g KOH in 0.05 mole of the appropriate alcohol and 70 ml xylene. The reaction mixture was heated until the ethyl or methyl alcohol ceased to distil off. The hot residue was filtered and slowly cooled. The crystals which separated were filtered off with suction, washed with cold petrol ether, and vacuum-dried. If crystals did not separate, the xylene was distilled off, and the residue repeatedly extracted with hot n-heptane. Alkoxysilatrane crystals came down when the total extracts cooled. 1-Benzoyloxysilatrane was purified by recrystallization from chloroform-n-heptane, and the other 1-alkoxysilatrane from n-heptane. The methoxy-, cyclohexoxy-, and benzyloxy- compounds were also crystallized, but from xylene. Runs without a catalyst were similarly carried out.

By way of example, three typical syntheses will be described.

1-Methoxysilatrane. Slow distillation (over 1 hr) of a mixture of 7.61 g (0.05 mole) tetramethoxysilane, 7.46 g (0.05 mole) triethanolamine, 0.1 g KOH, and 70 ml xylene gives 6.0 ml methanol (98% theoretical), boiling at 67°. The hot solution is filtered and slowly cooled to room temperature. The crystals formed are filtered off with suction, washed with cold petrol ether, and vacuum-dried. Yield 9.08 g, or 89% of theoretical, of 1-methoxysilatrane, melting at 152-154°. After a few recrystallizations from n-heptane the mp is 155-156°.

1-Tert. -butoxysilatrane. A mixture of 7.61 g (0.05 mole) tetramethoxysilane, 7.46 g (0.05 mole) triethanolamine, 3.71 g (0.05 mole) tert. -butanol, 0.1 g KOH, and 70 ml xylene are boiled for 45 min until the methanol (9.0 ml) distills over. The reaction mixture is filtered hot, and when the filtrate has cooled below 100°, 100 ml n-heptane are added. The crystals formed are worked up as in the preceding example. Yield 7.56 g. A further 0.55 g substance is obtained after distilling the solvent off from the mother liquors. Total yield 8.11 g or 66% of theoretical. The substance is found to undergo partial decomposition when recrystallized from n-heptane (some non-melting polymer insoluble in hot heptane is formed). After a few recrystallizations from n-heptane, 1-tert. -butoxysilane melts at 146.5-147.5°.

1-n-Amoxysilatrane. A mixture of 10.42 g (0.05 mole) tetraethoxysilane, 7.46 g (0.05 mole) triethanolamine, 4.41 g (0.05 mole) n-amyl alcohol, 0.1 g KOH, and 70 ml xylene is heated as in the previous examples. In 70 min 12.5 mole ethanol (theoretical 11.7 ml), boiling at 80° and containing a small amount of xylene, distills over. The hot solution is then filtered, and most of the xylene distilled off. The residue is repeatedly distilled, extracted with hot n-heptane. On cooling slowly crystals of 1-n-amoxysilatrane separate and are worked up in the usual way. Yield of material melting at 95-96°, 32 g or 63% of theoretical. After a few recrystallizations from n-heptane the substance melts at 102.5-103.5°.

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