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ATRANES

VIII. 1-Aroxysilatranes*

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A method of synthesizing hitherto unknown 1-aroxysilatranes $ROSi(OCH_2CH_2)_3N$ (R = aryl) is worked out.

It is based on transesterification of lower tetraalkoxysilanes with an equimolecular mixture of triethanolamine and the appropriate phenol (naphthol). Using the method, 12 compounds of the indicated type have been prepared and characterized, the yields in the main exceeding 90%.

The method which we previously worked out for synthesizing 1-organoxysilatranes [2] is based on transesterification of lower tetraalkoxysilanes by an equimolecular mixture of triethanolamine and the appropriate organic hydroxyl compound, and it was successfully applied to preparing 1-alkoxysilatranes [3]. The present paper describes the results of applying the method to the synthesis of hitherto unknown 1-aroxysilatranes (I), according to the equation:

$$ROH + Si(OR')_4 + (HOCH_2CH_2)_3N \rightarrow ROSi(OCH_2CH_2)_3N + 4R'OH,$$

where R = aryl, R' = Me, Et.

Synthesis of I is effected by heating equimolecular quantities of tetraethoxysilane (or tetramethoxysilane), triethanolamine, the appropriate phenol (or naphthol), an inert solvent (xylene, toluene and the like), along with a catalytic quantity of an alkali metal hydroxide (or without a catalyst), the ethanol (methanol) formed in the reaction being completely distilled off. The 1-aroxysilatranes crystallize out directly from the reaction products when they cool, or separate in the precipitate during the reaction, and are purified by recrystallization.

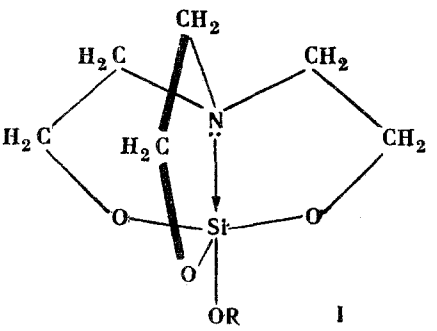
The yields and melting points of the I compounds prepared in this way, as well as analytical data for them, are given in the table.

Use of an alkali metal hydroxide as catalyst in the synthesis of I does not play the same fundamental part as in the preparation of 1-alkoxysilatranes [3]. With phenol and its alkyl derivatives, use of alkali increases the yield of the corresponding I by 5-40%, while, in the case of the nitrophenoxysilatranes, its use cuts the yield (by 4-25%).

The yields of the I compounds were mostly over 90%. Exceptions were 1-o-nitrophenoxy- and 1-(2', 4', 6'-trinitrophenoxy) silatrane, for which the yields were respectively 56 and 28%, and the 2', 4', 6'-trinitrophenoxy derivative, which it was quite impossible to synthesize. Evidently this is due to steric hindrance due to substituents ortho to the hydroxyl group in the starting phenols. It also proved impossible to obtain 1-p-aminophenoxysilatrane in the way described.

The I compounds prepared are colorless crystalline compounds (except the yellow 1-nitrophenoxysilatranes) with high melting points. They are readily soluble in halogenated hydrocarbons, dimethylformamide, and acetonitrile. Their solubilities in other solvents, among them water, are much lower than those of the 1-alkoxysilatranes.

The molecular weights of 1-phenoxy- and 1-cresoxysilatranes, found cryoscopically in nitrobenzene, are those of monomers. It is quite interesting that the molecular weights of most of the other aroxysilatranes investigated are 10-50% low, both in nitrobenzene and in benzene.



I

*For Part VII see [1].

1-Aroxysilatranes $RO\overset{\uparrow}{Si}(OCH_2CH_2)_3\overset{|}{N}$

R	Compound	Mp, °C (recrystallization solvent)	Formula	Found, %				Calculated, %				Unpurified material yield, %
				Si	C	H	N	Si	C	H	N	
C_6H_5	1-Phenoxysilatrane	228—229.5 ($CHCl_3+CCl_4$)	$C_{12}H_{17}NO_4Si$	10.44 10.51	54.12	6.75	5.36	10.50	53.91	6.41	5.24	99 89*
2-$CH_3C_6H_4$	1-o-Cresoxysilatrane	218—219.5 (xylene)	$C_{13}H_{19}NO_4Si$	10.03 10.03	55.31	6.69	5.04	9.98	55.49	6.81	4.98	98 83*
3-$CH_3C_6H_4$	1-m-Cresoxysilatrane	162.5—163.5 (xylene)	$C_{13}H_{19}NO_4Si$	10.22 10.14	55.86	6.96	5.23	9.98	55.49	6.81	4.98	89 82*
4-$CH_3C_6H_4$	1-p-Cresoxysilatrane	188—189 ($CHCl_3$+n-heptane)	$C_{13}H_{19}NO_4Si$	9.73 9.97	55.30	7.05	5.15	9.98	55.49	6.81	4.98	98 56*
4-$(CH_3)_3CC_6H_4$	1-(p-tert-Butylphenoxyl) silatrane	252—253 ($CHCl_3$+n-heptane)	$C_{16}H_{25}NO_4Si$	8.89 8.89	58.95	7.64	4.31	8.68	59.41	7.79	4.33	70
5-CH_3-2-$(CH_3)_2CHC_6H_3$	1-(5'-Methyl-2'-isopropylphenoxy) silatrane	217.5—218.5 ($CHCl_3$+n-heptane)	$C_{16}H_{25}NO_4Si$	8.74 8.81	59.60	7.59	4.53	8.68	59.41	7.79	4.33	90 81*
4-ClC_6H_4	1-p-Chlorophenoxysilatrane	166—167 (xylene)	$C_{12}H_{16}ClNO_4Si$**	9.51 9.49	47.61	5.60	4.59	9.31	47.76	5.34	4.64	~100 ~100*
2,4,6-$Cl_3C_6H_2$		230—230.5 (xylene)	$C_{12}H_{14}Cl_3NO_4Si$***	7.48 7.47	38.69	3.88	4.06	7.58	38.88	3.81	3.78	28
2-$O_2NC_6H_4$	1-o-Nitrophenoxysilatrane	233—234 (xylene)	$C_{12}H_{16}N_2O_6Si$	9.20 9.35	45.93	5.33	8.73	8.99	46.14	5.16	8.65	58
3-$O_2NC_6H_4$	1-m-Nitrophenoxysilatrane	197.5—198.5 (xylene)	$C_{12}H_{16}N_2O_6Si$	9.10 9.16	46.50	5.13	8.69	8.99	46.14	5.16	8.65	87 91*
4-$O_2NC_6H_4$	1-p-Nitrophenoxysilatrane	182.5—184 (toluene)	$C_{12}H_{16}N_2O_6Si$	8.67 8.97	46.42	5.22	9.17	8.99	46.14	5.16	8.65	75 ~100*
2-$C_{10}H_7$	1-β-Naphthoxysilatrane	184.5—185.5 (EtOH)	$C_{16}H_{19}NO_4Si$	8.95 8.98	60.45	6.01	4.61	8.85	60.54	6.03	4.41	88

* No catalyst

** Found: Cl 11.98%. Calculated: Cl 11.75%.

*** Found: Cl 28.90%. Calculated: Cl 28.68%.

The presence of an intramolecular coordination link Si ← N (see the structural formula) in I is shown by their high dipole moments (1-phenoxysilatrane has μ = 7.13 D [5]), as well as by IR spectroscopy [6] and PMR data, which will be published in one of the later papers.

The physiological activity of 1-aroxysilatranes is somewhat lower than that of the 1-arylsilatranes. More particularly, 1-phenoxysilatrane is 500-fold less toxic than 1-phenylsilatrane, for which LD_{50} = 0.4 mg/kg [7]. The activities of the aroxysilatranes are greatly reduced by introduction of substituents (Me, Me_2CH, Cl, NO_2) into the aromatic ring. Below are given the LD_{50} results for white mice intraperitoneally injected with 1-aroxysilatranes:*

R	LD_{50}, mg/kg
C_6H_5	200
p-NC_6H_4	700
p-ClC_6H_4	1050
p-$CH_3C_6H_4$	1275
5-CH_3-2-$(CH_3)_2CHC_6H_3$	4000

Experimental

Starting materials. The triethanolamine used in the syntheses was commercial CP material, twice vacuum-distilled. Tetraethoxysilane (industrial) was purified by distilling twice over sodium. Commercial CP phenol or purified by distillation or crystallization.

Analyses. C and H in I were determined simultaneously by combustion in a stream of oxygen. N was determined by the micro-Dumas method, using nickel or cobalt oxide. Si was determined as SiO_2 by ashing a weighed sample of the I with mixed concentrated nitric and sulfuric acids.

Method of synthesis. Every example of I was synthesized by a method similar to that described [3] for 1-alkoxysilatranes. The crystals of 1-aroxysilatranes which separated from the reaction products were filtered off with suction, washed with ether (to remove residual phenol), and vacuum-dried.

Three syntheses are described below by way of examples.

1-Phenoxysilatrane. A mixture of 10.42 g (0.05 mole) tetraethoxysilane, 7.46 g (0.05 mole) triethanolamine, 4.70 g (0.05 mole) phenol, 0.1 g KOH, and 100 ml xylene was slowly distilled (through an 18 cm rod and disc column), and in an hour 12.5 ml EtOH (theory 11.7 ml) plus a small amount of xylene as impurity separated. The reaction products were a transparent yellow liquid, which, on cooling, deposited slightly yellowish crystals, and these were filtered off with suction, washed with ether, and vacuum-dried. Yield of crude 1-phenoxysilatrane mp 210–215° C 12.80 g. A further 0.40 g substance was obtained by distilling off the xylene from the filtrate. Total yield 13.20 g (99%). Repeated recrystallization from $CHCl_3$ + COl_4 or $CHCl_3$+n-heptane gave pure 1-phenoxysilatrane mp 228–229.5°, C, M 271; 258. Calculated for $C_{12}H_{17}NO_4SI$: M 267.36.

1-(2', 4', 6'-Trichlorophenoxy) silatrane. The EtOH was slowly distilled off from a mixture of 10.42 g (0.05 mole) tetraethoxysilane, 7.46 g (0.05 mole) triethanolamine, 0.1 g KOH, and 150 ml xylene. (In 1 hr 30 min 8.5 ml EtOH was obtained.) The reaction products were cooled, 9.87 g (0.05 mole) 2, 4, 6-trichlorophenol added, and heating resumed, a further 0.8 ml EtOH distilling over in 3 hr. Half of the xylene was then distilled off the homogeneous brown solution obtained; on cooling a gray precipitate formed, and this was worked up as described in the previous experiment. Yield of material mp 216–218°C, 4.44 g (28%). Three crystallizations from xylene gave completely white crystals of 1-(2', 4', 6'-trichlorophenoxy) silatrane mp 230–230.5° C.

1-β-Naphthoxysilatrane. The EtOH was slowly distilled off from a mixture of 10.42 g (0.05 mole) tetraethoxysilane, 7.46 g (0.05 mole) triethanolamine, 7.21 g (0.05 mole) β-naphthol, 0.1 g KOH, and 150 ml and 11.2 ml EtOH obtained in 1 hr 30 min. The reaction products formed two liquid layers. On cooling, the lower one solidified to a gray crystalline mass, and a quantity of grayish crystals separated from the upper one. Yield of 1-β-naphthoxysilatrane mp 170–172°C, 14.02 g (88%). Repeated recrystallization from dry EtOH or dry AcOEt gave the pure compound mp 184.5–185.5° C.

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