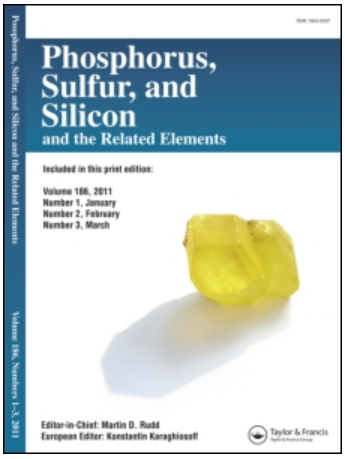

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SYNTHESIS AND CHARACTERIZATION OF 3-ETHYLSILATRANES

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SYNTHESIS AND CHARACTERIZATION OF 3-ETHYLSILATRANES

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A series of 1-Organyl-3-ethylsilatranes, $RSi(OCHEtCH_2)(OCH_2CH_2)_2N$, where R= $H_2N(CH_2)_3$-, $H_2N(CH_2)_2NH(CH_2)_3$-, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_3$-, $Cl(CH_2)_3$-, CH_2=CH-, $CH_3CONH(CH_2)_3$-, $H_2NCONH(CH_2)_3$-, $C_6H_9O(CH_2)_2$-, $C_3H_5N_2(CH_2)_3$-, $C_3N_3O_3(CH_2CH_2\text{-}CH_2)_3$- have been synthesised in yields ranging from 79 to 93% by transesterification of corresponding 1-organyltrialkoxysilanes with bis(2-hydroxyethyl)-2-hydroxybutylamine. These silatranes have been characterized by elemental analyses, IR, ^1H and ^{13}C NMR spectroscopy.

Keywords: Bis(2-hydroxyethyl)-2-hydroxybutylamine; transesterification; silatrane; NMR spectroscopy

INTRODUCTION

Among the compounds of pentacoordinated silicon, the silatranes, $RSi(OCH_2CH_2)_3N$, (1-organyl-2,8,9-trioxa-5-aza-1-silatricyclo [3,3,3, $0^{1,5}$] undecanes), are compounds with characteristic bonding structures, several representatives of which have biological activity[1–3]. 1-Organylsilatranes having C-substituted in the silatrane skeleton also exhibit biological activity which depends on the nature, position and the number of substituents present in the silatrane skeleton[3,4]. Silatranes with C-substituted (CH_3

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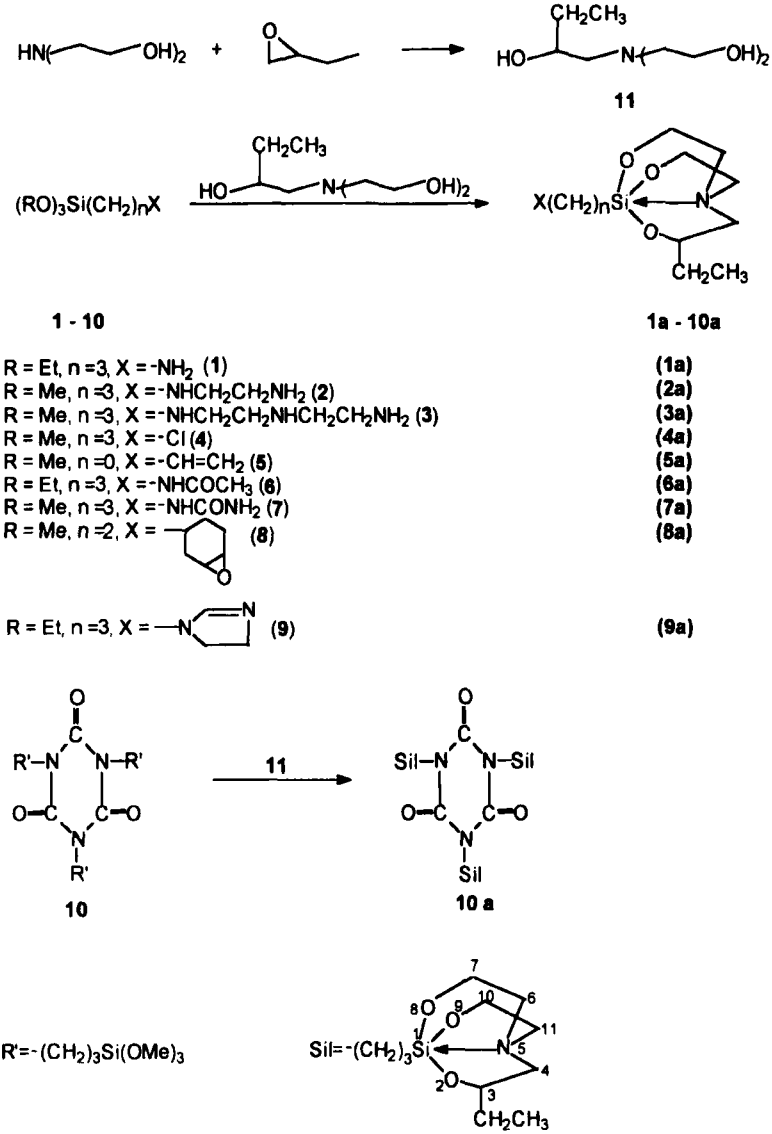
C_6H_5, CH_2Cl, CF_3) at 3,7 and/or 10 position of silatrane skeleton have been studied in great detail[3–6]. Diastereomeric study with methyl substituted at 3,7,10 and 4,4,7,10-positions of the atrane fragment of 1-vinyl-3,7,10-trimethyl[7]- and 1-vinyl-4,4,7,10-tetramethylsilatranes[8] as well as carboxylic substituted at position 4 have been carried out[9,10]. 4-Alkyl substituted silatranes have received little attention[11–13], whereas there are no reports to our knowledge of 3-ethylsilatrane derivatives so far. With our continued interest in the field of silatranes[14–27] we undertook the synthesis of 3-ethyl substituted silatranes and in the present work we report the preparation and spectroscopic investigation of a series of 3-ethylsilatranes. Our ultimate aim was the preparation and characterization of chiral 1-organyl-3-ethylsilatranes not known so far. However, in this paper the preparation and characterization of racemic-1-organyl-3-ethylsilatranes only are discussed.

RESULTS AND DISCUSSION

Transesterification of 1-organyltrialkoxysilanes (**1–10**) with bis(2-hydroxyethyl)-2-hydroxybutylamine, $N[(CH_2CH_2OH)_2(CH_2CHCH_2CH_3OH)]$ (**11**) gave Si-substituted 3-ethylsilatranes (**1a-10a**), respectively, in yields 79–93% in accordance with scheme 1. The compounds **1a-4a, 8a** and **9a** were purified by vacuum distillation while the pure compound **6a** was isolated as a viscous liquid. The compounds **5a** and **10a** were purified by recrystallization from $CHCl_3$ and petroleum ether (b.p. 40–60°C). All the compounds were well characterized by elemental analyses (table II), IR (table III), ^1H and ^{13}C NMR (table IV and V). ^1H and ^{13}C NMR spectra of compound **7a** were not recorded due to solubility problem. However, elemental analyses and IR spectra confirmed the proposed structure of compound **7a**. We have compared the ^1H and ^{13}C spectra of the 3-ethylsilatranes (**1a-10a**) with bis(2-hydroxyethyl)-2-hydroxybutylamine (**11**). The effect of the ethyl group at position 4 and 3 in the silatrane skeleton of compound **5a** was observed in the ^{13}C NMR spectra, whereas the melting point of compound **5a** was lower as compared to 1-vinyl-4-ethylsilatrane[12].



SCHEME 1 Synthesis of 3-ethylsilatranes

Infrared Spectra

Absorption frequencies of bonds of Si-substituted 3-ethylsilatranes (**1a-10a**) observed in the IR spectra fully substantiates the structures. The infrared spectroscopic investigation of silatranes for the structural fragment of Si-O-C-C is characterized by the typical frequencies appearing at 940–979, 1085–1114 cm^{-1} and a group of split bands in the region at 1117–1158 cm^{-1} [18,28]. The characteristic spectra for a pentacoordinated molecular structure were observed as medium intensity band at 572–590 cm^{-1}assigned to the bending vibration of silatrane skeleton as well as stretching vibration of the Si ← N coordinative bond indicating the coordination of the nitrogen atom to silicon[14,29,30]. The other absorption characteristics of the group appeared at 2962–2975 ($\nu_{as}CH_3$), 2861–2882 (ν_sCH_3)[31], 1440–1463 and 1360–1386 cm^{-1}(νCH_3-C) for CH_2-CH_3 group. The characteristic absorption frequencies of side groups for compounds **1a-10a** are cited in the text whereas the detailed IR spectral data of silatrane skeleton of 3-ethylsilatranes (**1a-10a**) are tabulated in table III.

TABLE I ^1H and ^{13}C NMR data (δ, ppm, $CDCl_3$) for $N[(CH_2CH_2OH)_2$-$(CH_2CHCH_2CH_3OH)]$

OH	*OCH*	*OCH_2*	*NCH_2*	*$OCCH_2$*	*CH_3*
5.41	3.76–3.50	d	2.66–2.08	1.55–1.33	1.06
(s,3H)	(m, 5H)		(m, 6H)	(m, 2H)	(t,3H, J=7.38 Hz)
	(69.98)	(59.87)	(57.97)	(28.0)	(10.41)
			(62.30)		

Numbers in parenthesis indicate ^{13}C NMR.
[d]Overlaps with OCH proton.

^1H NMR Spectra

In the ^1H NMR spectra of compound **11**, the OH proton appeared at 5.41 ppm as broad singlet while in the 3-ethylsilatranes (**1a-10a**) it has fully disappeared suggesting complete transesterification reaction of 1-organylsilanes (**1–10**) with compound **11**. OCH_2 and OCH as well as NCH_2 protons of compounds **1a-10a** appeared as complex multiplet at 3.85–3.28, 2.88–2.09 ppm, respectively. The pendant NCH_2 protons of compounds

1a-3a, 9a and **10a** overlap with NCH_2 protons of silatrane skeleton. The CH_2 and CH_3 protons of ethyl group appeared at higher field in case of 3-ethylsilatranes (**1a-10a**) as compared to CH_2 and CH_3 protons of bis(2-hydroxyethyl)-2-hydroxybutylamine (**11**). The $OCCH_2$ protons of ethyl group appeared as multiplet at 1.70–1.12 in compounds **1a-10a** and CH_3 protons of ethyl group appeared as a sharp triplet at 0.98–0.81 ppm in compounds **1a-9a** whereas it appeared as quartet in compound **10a**. The $OCCH_2$ protons appeared as multiplet at 1.55–1.33 whereas the CH_3 protons appeared as triplet at 1.06 ppm in the case of compound (**11**). $SiCH_2$ protons appeared as triplet in the region at 0.41–0.23 ppm in all compounds except compound **4a**. In compound **4a** it appeared as a multiplet. The ^1H NMR spectral data of side groups for compounds **1a-10a** are given in the text where as the detailed spectral data for silatrane skeleton are compiled in table IV.

^{13}C NMR Spectra

In the ^{13}C NMR, NCH_2 of compound **11** appeared as two peaks at δ 58.0 and 63.3 ppm. However, the peak appearing at 58.0 splits into two peaks and appeared in higher field at 52.3–51.7 and 51.7–51.2 ppm in the case of 3-ethylsilatranes (**1a-10a**)[32]. The appearance of two peaks of NCH_2 in compounds **11** suggest that out of three NCH_2 two are in same environment and three peaks of NCH_2 in compound **1a-10a** suggest different environment of all three NCH_2 carbon atoms. The ^{13}C NMR spectral data of compound **11** are given in table I. In the ^{13}C NMR of compounds (**1a-10a**), O<u>C</u>H appeared in the range at 69.5–67.4 (C-3), O<u>C</u>H_2 appeared in the range at 57.6–56.5 (C-7and C-10), N<u>C</u>H_2 appeared in the range at 56.0–54.9 (C-4), 52.3–51.7(C-6) and 51.7–51.2 (C-11), OC<u>C</u>H_2 appeared in the range at 28.3–26.8 and CH_3 at 9.9–9.0 ppm, respectively. Effect of substituted position of ethyl group observed in ^{13}C NMR spectra i.e. in case of 1-vinyl-4-ethylsilatrane, the OCH_2(3), NCH(4), NCH_2(6), OCH_2(7 and 10), NCH_2(11), CH_2 and CH_3 appeared at 61.9, 60.1, 45.6, 57.7, 49.2, 20.0 and 11.3 ppm, respectively[12], whereas in compound **5a**, the OCH(3), NCH_2(4), NCH_2(6), OCH_2 (7and10), NCH_2 (11), CH_2 and CH_3 appeared at 68.4, 56.0, 51.8, 57.3, 51.2, 27.9 and 9.6 ppm, respectively. The ^{13}C NMR spectral data of side groups for compounds (**1a-10a**) are cited in the text where as for silatrane skeleton they are tabulated in table V.

TABLE II Characterization details of 3-ethylsilatranes (**1a-10a**)

nds	*Empirical formula*	*Formula weight*	*M.P./B.P. °C (mm, Hg)*	*Yield (%)*	*Found (calculated) %*		
					C	*H*	*N*
	$C_{11}H_{24}N_2O_3Si$	260.41	185–87[a] (3)	89	50.95 (50.74)	9.15 (9.29)	10.70 (10.76)
	$C_{13}H_{29}N_3O_3Si$	303.48	230–32[a] (5)	92	51.23 (51.45)	9.83 (9.63)	13.99 (13.85)
	$C_{15}H_{34}N_4O_3Si$	346.55	232–34[a] (1.5)	93	52.21 (51.98)	9.71 (9.88)	15.98 (16.16)
	$C_{11}H_{22}NO_3SiCl$	279.89	170–72[a] (2)	93	46.98 (47.20)	8.10 (7.92)	4.91 (5.01)
	$C_{10}H_{19}NO_3Si$	229.36	85–87	79	52.61 (52.37)	8.55 (8.35)	6.01 (6.11)
	$C_{13}H_{26}N_2O_4Si$	302.45	viscous liquid	83	51.49 (51.63)	8.88 (8.67)	9.14 (9.26)
	$C_{12}H_{25}N_3O_4Si$	303.44	185–87[b]	91	47.19 (47.50)	8.17 (8.30)	14.10 (13.85)
	$C_{16}H_{29}NO_4Si$	327.50	230–32[a] (5)	89	58.92 (58.68)	9.11 (8.93)	4.33 (4.28)
	$C_{14}H_{27}N_3O_3Si$	313.47	240–41[a] (6)	86	53.39 (53.64)	8.91 (8.68)	13.21 (13.40)
	$C_{36}H_{66}N_6O_{12}Si_3$	859.22	170–71	84	50.53 (50.32)	7.94 (7.74)	9.62 (9.78)

point.
position point

TABLE III Absorption frequencies of bonds of silatrane skeleton in 3-ethylsilatranes (**1a-10a**)

unds	*1a*	*2a*	*3a*	*4a*	*5a*	*6a*	*7a*	*8a*	*9a*
$_2$N)	1385m	1400w	1380m	1380w	1400m	1400w	1400w	1380m	1400m
	1357m	1357m	1357m	1358m	1360w	1371m	1347m	1361m	1361m
$_2$O)	1277s	1278s	1276s	1272s	1273m	1292m	1272m	1278s	1280s
$_2$O)	1175m	1176m	1177m	1180m	1180m	1197m	1202m	1170m	1176m
O)	1140vs	1135vs	1150vs	1135vs	1140s	1130vs	1135vs	1140vs	1145vs
	1102vs	1107vs	1104vs	1105vs	1097vs	1095vs	1096vs	1108vs	1106vs
)	1059s	1059s	1059s	1058s	1050w	1035vs	1027vs	1059s	1058s
	1009s	1009s	1008s	1008s	1000s	1003s	1001s	1008s	1008s
C)	990m	985m	986s	970s	980m	972s	975s	985s	985s
	928m	930m	928s	940m	939m	920m	935w	927s	927s
C)	902s	902s	904s	904s	900m	903m	902m	900s	905s
N)	880s	885s	884s	880m	881m	880m	880w	884s	880m
O)	815vs	820vs	813vs	810s	830m	810m	830w	813vs	815vs
	780vs	785vs	794vs	773s	780s	782s	780m	795vs	798vs
	759vs	766vs	763vs	760s	760s	760s	760s	769vs	770vs
-O)	721s	721s	720s	720m	725s	725m	720m	725s	719s
	672m	673m	674w	670m	673s	693m	673s	680s	673s
	628m	627m	628m	620m	635m	630m	634m	626m	631m
– N)	575m	575m	576m	580m	575m	580m	590m	575m	572m

, s:strong, vs:very strong, w:weak.

TABLE IV ^{1}H NMR Spectral data (δ, ppm) of 3-ethylsilatranes (**1a-10a**)

ads	*Atrane Skeleton*				*SiCH$_2$*	*CCH$_2$C*	*CH$_2$-N*	*C*
	OCH$_2$ & OCH	*NCH$_2$*	*OCCH$_2$*	*CH$_3$*				
	3.77 – 3.50	2.83 – 2.21	1.54 – 1.36	0.94	0.38	[a]	[b]	
	(m,5H)	(m,8H)	(m,4H)	(t,3H,J=7.25)	(t,2H,J=8.25)			
	3.74 – 3.51	2.82 – 2.25	1.62 – 1.38	0.95	0.40	[a]	[b]	
	(m,5H)	(m,12H)	(m,4H)	(t,3H,J=7.50)	(t,2H,J=8.25)			
	3.61 – 3.49	2.71 – 2.09	1.36 – 1.27	0.81	0.23	1.50–1.39	[b]	
	(m,5H)	(m,16H)	(m,2H)	(t,3H,J=7.38)	(t,2H,J=8.14)	(m,2H)		
	3.54 – 3.28	2.32 – 1.63	1.37 – 1.12	0.93	0.89–0.84	b	–	3
	(m,5H)	(m,8H)	(m,2H)	(t,3H,J=7.29)	(m,2H)			(t,2H
	3.85 – 3.74	2.88 – 2.33	1.70 – 1.45	0.98	–	–	–	
	(m,5H)	(m,6H)	(m,2H)	(t,3H,J=7 25)				
	3.71 – 3.60	2.80 – 2.39	1.60 – 1.45	0.95	0.40	1.50 – 1.41	2.21–2.05	
	(m,5H)	(m,6H)	(m,2H)	(t,3H,J=7.50)	(t,2H,J=7.89)	(m,2H)	(m,2H)	
	3.72 – 3.62	2.79 – 2.60	1.36 – 1.39	0.94	0.34	[a]	–	
	(m,5H)	(m,6H)	(m,4H)	(t,3H,J=7.61)	(t,2H,J=7.83)			
	3.77 – 3.67	2.83 – 2.26	1.25 – 1.41	0.96	0.37	1.65–1.58	3.07–3.18	
	(m,5H)	(m,8H)	(m,2H)	(t,3H,J=7.50)	(t,2H,J-8 25)	(m,2H)	(t,2H,J=7.5)	
	3.81 – 3.55	2.79 – 2.24	1.52 – 1.40	0.95	0.41	1.73–1.66	[b]	
	(m,5H)	(m,24H)	(m,6H)	(q,9H,J=8.33)	(t,6H,J=8.0)	(m,6H)		

s with $OCCH_2$ protons.
s with NCH_2 protons, J values are in Hz.

TABLE V ^{13}C NMR Spectral data (δ, ppm) of 3-ethylsilatranes (**1a-10a**)

nds	*Atrane Skeleton*							*SiCH₂*	*CCH₂C*	*CH₂-N*
	OCH (3)	*OCH₂ (7&10)*	*NCH₂ (4)*	*NCH₂ (6)*	*NCH₂ (11)*	*OCCH₂*	*CH₃*			
	68.5	57.6	56.0	51.8	51.3	27.6	9.6	12.9	29.5	45.3
	69.5	57.3	55.5	52.3	51.7	27.4	9.9	10.6	23.4	41.4
	67.4	56.5	54.9	52.1	51.5	26.8	9.0	12.6	24.2	40.7
	68.5	57.5	55.8	51.7	51.2	28.3	9.9	15.0	30.0	–
	68.4	57.3	56.0	51.8	51.2	27.9	9.6	–	–	–
	68.3	57.5	55.9	52.1	51.3	26.9	9.7	12.9	25.2	43.2
	67.5	57.5	55.8	51.8	51.2	27.1	9.5	12.6	24.1	–
	68.5	57.5	56.0	51.8	51.3	27.8	9.6	13.1	24.2	48.0
	68.5	57.6	56.0	51.9	51.4	27.8	9.7	13.0	23.4	45.7

EXPERIMENTAL

Melting points and boiling points are uncorrected. All the operations were carried out under argon atmosphere. 1-Organyltrialkoxysilanes i.e. 3-aminopropyltriethoxy-(**1**) (Aldrich), 3-(2-aminoethylaminopropyl)trimethoxy-(**2**)(Fluka), 3-[2-{(2-aminoethyl)aminoethyl}aminopropyl] trimethoxy- (**3**) (Fluka), 3-chloropropyltrimethoxy- (**4**) (Fluka), vinyltrimethoxysilanes (**5**) (Fluka), N-[3-(trimethoxysilyl)propyl]urea(**7**) (Aldrich), 2-[(3,4-epoxycyclohexyl)ethyl]trimethoxysilane (**8**)(Fluka), 1-[3-(triethoxysilyl)propyl]-2-imidazoline (**9**) (Fluka), tris[3-(trimethoxysilyl)propyl]isocyanurate (**10**) (Aldrich) were used as received. N-[3-(triethoxysilyl)propyl]acetamide (**6**) was prepared as described in the literature[33]. 1,2-Epoxybutane (Fluka) and KOH(LR) were used as such. Diethanolamine (LR) was vacuum distilled before use. Reagent grade solvents were dried and purified by conventional methods. Petroleum ether (b.p. 40–60°C) was distilled and dried over sodium wire immediately before use. ^{1}H and ^{13}C NMR spectra were recorded on Jeol 90 FX (90 MHz), Brucker DPX 300 (300 MHz) and Brucker (500 MHz) instruments using TMS as internal reference. Chemical shifts are quoted in ppm down field from TMS. Infrared spectra were recorded using KBr pellets and nujolmull in the range 4000–500 cm^{-1}on a Nicolet Magna 750 FTIR spectrophotometer. C, H and N analyses were carried out on Elemental analyser system GmbH analyser, Vario El. Melting points were determined on a Toshniwal melting point apparatus.

Synthesis of bis(2- hydroxyethyl)-2-hydroxybutylamine(11)

Compound **11** was obtained by N-alkylation of diethanolamine with 1,2-epoxybutane (scheme 1). To diethanolamine (10.5 g, 100 mmol) taken in a three necked round bottom flask was added 1,2-epoxybutane (7.21 g, 100 mmol) dropwise with constant stirring at room temperature. Reaction became slightly exothermic after 1 hour. Stirring of reaction mixture was continued for further 3–4 hours. Compound **11** was vaccum distilled. B.p. 159–160°C/0.9 mm Hg. Yield (10.60 g, 82%). Elemental analysis: Anal. Calc: C, 54.51; H, 10.81; N 7.90. Found: C, 54.81; H, 10.63; N, 7.81 for $C_8H_{19}NO_3$. IR (nujolmull, cm^{-1}): 3354br(νOH), 2957s($\nu_{as}CH_3$), 2950vs($\nu_{as}CH_2$), 2879s(ν_sCH_2O), 2818s (ν_sCH_2N), 1457s(δ_sCH_2O),

1390m(νCH), 1360m(ωCH$_2$N), 1280m(ωCH$_2$O), 1160m(τCH$_2$O), 1140m(νC-O), 1076vs, 1046vs(ν$_{as}$NC$_3$), 908s(ν$_s$NC$_3$), 878s(νC-N).

Synthesis of N-[3-(triethoxysilyl)propyl]acetamide(6)

A mixture of (15.47 g, 70 mmol) of compound **1** and (4.13 g, 70 mmol) of acetamide in presence of catalytic amount of ammonium sulphate was heated to reflux for 18 hours at 150–160°C and distilled in vacuum. The yield of $H_3CCONH(CH_2)_3Si(OC_2H_5)_3$, (16.5g, 90%); B.p. 196–198°C/6 mm Hg. Elemental Analysis: Anal. Calc: C, 50.15; H, 9.57; N, 5.32; Si, 24.30. Found: C,50.33; H,9.73; N, 5.23; Si, 24.13 for $C_{11}H_{25}NO_4Si$. IR (nujolmull, cm^{-1}): 3293br(ν$_{as}$NH), 3089s(ν$_s$NH), 2975vs(ν$_{as}$CH$_3$), 2930vs(ν$_{as}$CH$_2$), 2887vs (ν$_s$CH$_2$, ν$_s$CH$_3$), 1656vs(νC=O), 1558s(δNH), 1479w, 1442s, 1388s, 1371s(δC-CH$_3$), 1293s(ωCH$_2$O), 1194s (τCH$_2$O), 1166vs, 1116vs, 1078vs, 957s(ννSi-O-C-C), 882w(νC-N), 791vs(ν$_{as}$Si-O), 703w, 682w and 602s(ν$_s$Si-O). ^{1}H NMR (δ,CDCl$_3$): 0.61(t,2H, CH$_2$Si,J=6.75Hz), 1.23(t,3H,CH$_3$C,J=6.39Hz), 1.60(m,2H,C-CH$_2$-C), 1.94(s,3H,COCH$_3$), 3.22(m,2H,NCH$_2$-C), 3.87(q,2H, OCH$_2$), 6.55 (s,1H,NH).

General Synthetic Procedure for 3-ethylsilatranes (1a-10a)

The reactions were conducted in a three necked round bottom flask fitted with a dropping funnel and reflux condenser and mounted on a magnetic stirrer. Bis(2-hydroxyethyl)-2-hydroxybutylamine (**11**) and catalytic amount of KOH were taken in benzene or toluene and to this equimolar amount of silanes in corresponding solvent was added dropwise during 15 min. with stirring at room temperature. The solution was heated to reflux. The alcohol formed during course of the reaction was distilled off and reaction mixture was concentrated by removal of solvent. The products were purified by recrysrallization or by vacuum distillation. Characterization details of compounds **1a-10a** are listed in table II.

3-Aminopropyl-3-ethylsilatrane (1a)

Compound **1a** was obtained by stirring and refluxing a solution of compound **1** (4.42 g, 20 mmol) and compound **11** (3.54 g, 20 mmol) in 25 mL

toluene containing KOH as catalyst for 6 hours. Yield (4.62 g, 88.7%); B.p. 185–187°C/3 mm Hg. IR (nujolmull, cm^{-1}): 3365s($\nu_{as}NH$), 3297s($\nu_{s}NH$), 2972vs($\nu_{as}CH_3$), 2861s($\nu_{s}CH_3$), 1593m(δNH_2), 1457s, 1385m(δCH_3C). ^1H NMR (δ, $CDCl_3$): 1.54 (s, 2H, NH_2)

1-[N-(2-Aminoethyl)aminopropyl]-3-ethylsilatrane (2a)

Compound **2a** was obtained by stirring and refluxing a solution of compound **2** (4.45 g, 20 mmol) and compound **11** (3.54 g, 20 mmol) in 25 mL toluene containing KOH as catalyst for 3 hours. Yield (5.57 g, 91.8%); B.p. 230–232°C/5 mm Hg. IR(nujolmull, cm^{-1}): 3366s($\nu_{as}NH$), 3303s($\nu_{s}NH$), 2970vs($\nu_{as}CH_3$), 2872s($\nu_{s}CH_3$), 1598m(δNH_2), 1457s, 1386 m(δCH_3C); ^1H NMR (δ,$CDCl_3$): 1.55 (s, 3H, NH & NH_2); ^{13}C NMR (δ, $CDCl_3$): 52.60 ($NH\underline{C}H_2CH_2$), 53.0($CH_2\underline{C}H_2NH_2$).

3-[2-{(2-Aminoethyl)aminoethyl}aminopropyl]-3-ethylsilatrane (3a)

Compound **3a** was obtained by stirring and refluxing a solution of compound **3** (26.54 g, 100 mmol) and compound **11** (17.70 g, 100 mmol) in 55 mL benzene containing KOH as catalyst for 3 hours. Yield (32.34 g, 93.3%); B.p. 232–234°C/1.5 mm Hg. IR (nujolmull, cm^{-1}): 3359s($\nu_{as}NH$), 3299s($\nu_{s}NH$), 2972vs($\nu_{as}CH_3$), 2872vs($\nu_{s}CH_3$), 1600m (δNH_2), 1457s, 1380m(δCH_3C); ^1H NMR(δ,$CDCl_3$): 1.71(s, 4H, NH & NH_2); ^{13}C NMR (δ, $CDCl_3$): 48.12($NH\underline{C}H_2CH_2$), 48.34($NHCH_2\underline{C}H_2$),50.24($\underline{C}H_2CH_2NH_2$),50.75 ($CH_2\underline{C}H_2NH_2$).

3-Chloropropyl-3-ethylsilatrane (4a)

Compound **4a** was obtained by stirring and refluxing a solution of compound **4** (9.93 g, 50 mmol) and compound **11** (8.85 g, 50 mmol) in 100 mL benzene containing KOH as catalyst for 2 hours. Yield (12.93g, 92.5%); B.p. 170–172°C/2mm Hg. IR(nujolmull, cm^{-1}): 2963vs($\nu_{as}CH_3$), 2875s($\nu_{s}CH_3$), 1457s, 1380m(δCH_3C), 623s(νC-Cl).

1-Vinyl-3-ethylsilatrane (5a)

Compound **5a** was obtained by stirring and refluxing a solution of compound **5** (8.0 g, 54 mmol) and compound **11** (9.52 g, 54 mmol) in 30 mL toluene containing KOH as catalyst for 4 hours. Yield (9.77 g, 78.9%);

M.p. 85–87°C. IR (KBr pellet, cm^{-1}): 3047s(νCH), 2970vs($\nu_{as}CH_3$), 2882s(ν_sCH_3), 1603s(νC=C), 1457s, 1370m(δCH_3C); ^1H NMR(δ, $CDCl_3$): 5.76–6.04 (m,3H,CH and CH_2); ^{13}C NMR (δ, $CDCl_3$): 129.10 (CH_2), 139.81(CH).

N-[3-(3-Ethylsilatranyl)propyl)]acetamide (6a)

Compound **6a** was obtained by stirring and refluxing a solution of compound **6** (0.52 g, 2 mmol) and compound **11** (0.35 g, 2 mmol) in 25 mL benzene containing KOH as catalyst for 3 hours. Yield (0.50 g, 83.3%) and obtained as a viscous liquid. IR (nujolmull,cm^{-1}): 3289s ($\nu_{as}NH$), 3092s (ν_sNH), 2970vs ($\nu_{as}CH_3$), 2878s (ν_sCH_3), 1636vs (νC=O), 1557m(δNH), 1440s, 1371m(δCH_3C); ^1H NMR (δ,$CDCl_3$): 1.93 (s,3H,CH_3), 6.60 (s, 1H, NH); ^{13}C NMR (δ, $CDCl_3$): 23.5 (CH_3), 169.8 (C=O).

N-[3-(3-Ethylsilatranyl)propyl]urea (7a)

Compound **7a** was obtained by stirring and refluxing a solution of compound **7** (4.45 g, 20 mmol) and compound **11** (3.54 g, 20 mmol) in 25 mL toluene containing KOH as catalyst for 8 hours. Yield (5.50 g, 90.6%); M.p. 185–187°C (decomposes). IR (KBr pellet,cm^{-1}): 3417s ($\nu_{as}NH$), 3353s (ν_sNH), 2972vs ($\nu_{as}CH_3$), 2878vs (ν_sCH_3) 1651vs (νC=O), 1591m(δNH1°), 1553m(δNH2°), 1443s, 1380m(δCH_3C).

2-[(3,4-Epoxycyclohexyl)ethyl]-3-ethylsilatrane (8a)

Compound **8a** was obtained by stirring and refluxing a solution of compound **8** (4.18 g, 17 mmol) and compound **11** (3.0 g, 17 mmol) in 25 mL toluene containing KOH as catalyst for 2 hours. Yield (4.91 g, 88.7%); B.p. 230–232°C/5 mm Hg. IR (nujolmull, cm^{-1}): 2965vs($\nu_{as}CH_3$), 2872s(ν_sCH_3), 1645w, 1542w(epoxycyclohexane ring), 1455s, 1361m(δCH_3C); ^1H NMR (δ,$CDCl_3$): 0.79–2.22 (m, 9H, epoxycyclohexane ring); ^{13}C NMR (δ $CDCl_3$): 25.83, 31.27, 35.44, 51.81, 52.25, 53.10 (epoxycyclohexane ring).

1-[3-(3-Ethylsilatranyl)propyl]-2-imidazoline (9a)

Compound **9a** was obtained by stirring and refluxing a solution of compound **9** (5.50 g, 20 mmol) and compound **11** (3.50 g, 20 mmol) in 25 mL

toluene containing KOH as catalyst for 2 hours. Yield (5.38 g, 85.8%); B.p. 240–241°C/6 mm Hg. IR (nujolmull, cm^{-1}): 2962vs($\nu_{as}CH_3$), 2871s(ν_sCH_3), 1668m, 1601w(imidazoline ring), 1457s, 1361m(δ CH_3C); ^1H NMR (δ,$CDCl_3$): 6.80(s,1H,CH), 3.22(t,4H,CH_2,J=10.0Hz) (imidazoline ring); ^{13}C NMR (δ, $CDCl_3$): 157.9 (C-2), 54.5 (C-4), 50.5 (C-5).

Tris[3-(3-Ethylsilatranyl)propyl]isocyanurate (10a)

Compound **10a** was obtained by stirring and refluxing a solution of compound **10** (3.08 g, 5 mmol) and compound **11** (2.66 g, 15 mmol) in 25 mL toluene containing KOH as catalyst for 5 hours. Yield (3.60 g, 83.8%); M.p. 170–171°C. IR (KBr, cm^{-1}): 2964vs ($\nu_{as}CH_3$), 2875s(ν_sCH_3), 1688vs(νC=O), 1463s, 1360m(δCH_3C). ^{13}C NMR (δ, $CDCl_3$): 148.98 (C=O).

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