A Novel Synthesis of 2,4,10-Trioxa-3-silaadamantanes[1]

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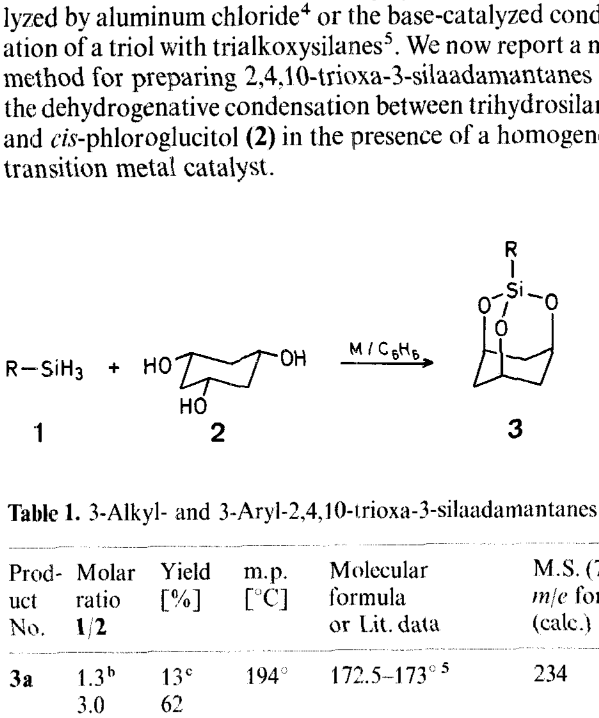
It has been recently found that a variety of adamantyl derivatives reveal unique physiological activities[2]. In this connection, the preparation of silicon-containing heteroadamantanes and related cage compounds such as silatranes is of interest[3] and some of them have already been obtained by the isomerization of silicon-containing cyclic compounds catalyzed by aluminum chloride[4] or the base-catalyzed condensation of a triol with trialkoxysilanes[5]. We now report a novel method for preparing 2,4,10-trioxa-3-silaadamantanes **3** by the dehydrogenative condensation between trihydrosilanes **1** and *cis*-phloroglucitol (**2**) in the presence of a homogeneous transition metal catalyst.



1 **2** **3**

For the purpose of condensation between phenylsilane **1a** and **2**, transition metal complexes such as chloroplatinic acid, dichlorobis[triphenylphosphine]platinum or chlorotris[triphenylphosphine]rhodium were effective and gave the expected silaadamantane **3a**[5]. However, use of dichlorobis[triphenylphosphine]nickel or dichlorobis[triphenylphosphine]palladium as catalyst did not give a satisfactory result (Table 1). Among these catalysts, it has been found that the yield of **3a** with the Wilkinson catalyst was best (62 % after sublimation). The yield of **3** depends on the ratio of **1** to **2** and it is remarkable that a high ratio of **1** to **2** gives rather satisfactory results. This is the first example of preparing a cage compound by the "one-pot" dehydrogenative intermolecular condensation between three reaction sites of two reagents catalyzed by a transition metal.

It is also noteworthy that the substituent effect of **3** on the ^{29}Si-N.M.R. chemical shift shows a similar trend, though to a small extent, to that of aryltriethoxysilanes[6] (Table 1).

The synthetic utility of the present method for the preparation of cage compounds **3** is seen in the ready accessibility of the starting materials and simple experimental manipulation.

Alkyl- and Arylsilanes 1:

The trihydrosilanes **1** (Table 2) were obtained by reduction of the corresponding trichlorosilanes[7–15] with lithium aluminum hydride in ether according to the reported procedure[16].

cis-Phlorogucitol (2):

This compound was prepared according to the literature procedure[17]; m.p. 182 °C (Lit.[17], m.p. 185 °C).

^{13}C-N.M.R. (acetone-d_6): δ = 66.71 (d), 46.22 ppm (t).

3-Alkyl- and 3-Aryl-2,4,10-trioxa-3-silaadamantanes 3; General Procedure:

The trihydrosilane **1** (10–30 mmol, see Table 2) is added dropwise to a suspension of *cis*-phloroglucitol (**2**; 1.32 g, 10 mmol) and the catalyst tris[triphenylphosphine]rhodium(I) chloride[25] (46 mg, 0.05 mmol) in benzene (400 ml). After 15–18 h, the mixture is concentrated to ~ 30 ml and transferred to a sublimation apparatus. After the solvent is evaporated under reduced pressure, the residue is subjected to sublimation at 100 °C/0.005 torr. The sublimate is recrystallized from *n*-hexane to give **3** (Table 1).

Table 1. 3-Alkyl- and 3-Aryl-2,4,10-trioxa-3-silaadamantanes **3** prepared[a]

Product No.	Molar ratio **1**/**2**	Yield [%]	m.p. [°C]	Molecular formula or Lit. data	M.S. (70 eV) m/e for M⁺ (calc.)	^{1}H-N.M.R. (CCl_4/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{29}Si-N.M.R. ($CDCl_3$) δ [ppm]
3a	1.3[b] 3.0 1.3[d]	13[c] 62 49[e]	194°	172.5–173°[5]	234	1.7 (d, 3H, J = 14 Hz); 2.7 (d, 3H, J = 14 Hz); 4.5 (br. s, 3H); 7.2–7.7 (m, 5H)	37.47 (t); 71.28 (d); 125.4 (s); 128.07 (d); 132.12 (d); 134.08 (d)	−41.97
3b	2.6	40	188°	$C_{12}H_{13}ClO_3Si$ (268.8)	268.0312[g] (268.0322)	1.8 (d, 3H, J = 15 Hz); 2.7 (d, 3H, J = 15 Hz); 4.7 (br. s, 3H); 7.6 (d, 2H, J = 9 Hz); 7.7 (d, 2H, J = 9 Hz)	37.4 (t); 71.41 (d); 123.7 (s); 128.47 (d); 135.52 (d); 138.46 (s)	−41.97
3c	2.1	43	223°	$C_{15}H_{22}O_3Si_2$[h] (306.5)	306	0.3 (s, 9H); 1.8 (d, 3H, J = 14 Hz); 2.73 (d, J = 14 Hz, 3H); 4.58 (br. s, 3H); 7.3–7.7 (m, 4H)	1.44 (q); 37.4 (t); 71.22 (d); 125.46 (s); 132.71 (d); 133.04 (d); 145.44 (s)	−41.97
3d	2.3	54	205°	$C_{13}H_{16}O_3Si$[h] (248.4)	248	1.86 (d, 3H, J = 14 Hz); 2.4 (s, 3H); 2.83 (d, 3H, J = 14 Hz); 4.75 (br. s, 3H); 7.2–7.8 (m, 4H)	21.80 (q); 37.47 (t); 71.22 (d); 121.97 (s); 128.86 (d); 134.08 (d); 142.4 (s)	−41.48

Table 1. (Continued)

Product No.	Molar ratio **1**|**2**	Yield [%]	m.p. [°C]	Molecular formula or Lit. data	M.S. (70 eV) *m/e* for M$^+$ (calc.)	^{1}H-N.M.R. (CCl_4/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{29}Si-N.M.R. ($CDCl_3$) δ [ppm]
3e	2.0	55	258°	$C_{16}H_{22}O_3Si$[h] (290.4)	290	1.4 (s, 9H); 1.9 (d, 3H, *J* = 14 Hz); 2.82 (d, 3H, *J* = 14 Hz); 4.7 (br. s, 3H); 7.4–7.8 (m, 4H)	30.94 (q); 34.79 (s): 37.34 (t). 71.09 (d); 122.0 (s); 124.87 (d); 133.88 (d); 155.29 (s)	−41.56
3f	1.4	32[i]	166°	$C_{13}H_{16}O_4Si$[h] (264.4)	264	1.43 (d, 3H, *J* = 14 Hz); 2.65 (d, 3H, *J* = 14 Hz); 3.75 (s, 3H); 4.28 (br. s, 3H); 6.91 (d, 2H, *J* = 9 Hz); 7.62 (d, 2H, *J* = 9 Hz)	37.47 (t); 55.03 (q); 71.22 (d); 113.84 (d); 116.52 (s); 135.91 (d); 162.67 (s)	−41.31
3g	1.9	34	218°	$C_{14}H_{19}NO_3Si$ (277.5)	277.1117[g] (277.1132)	1.73 (d, 3H, *J* = 14 Hz); 2.7 (d, 3H, *J* = 14 Hz); 3.0 (s, 6H); 4.53 (br. s. 3H); 6.55 (d, 2H, *J* = 8 Hz); 7.37 (d, 2H, *J* = 8 Hz)	37.34 (q); 39.69 (t); 70.96 (d); 109.93 (s); 111.23 (d); 135.12 (d); 152.62 (s)	−40.49
3h	1.0	25[i]	108°	$C_{13}H_{16}O_3Si$ (248.4)	248.0859[g] (248.0867)	1.68 (d, 3H, *J* = 13 Hz); 2.22 (s, 2H); 2.53 (d, 3H, *J* = 13 Hz); 4.42 (br. s, 3H); 7.0–7.2 (m, 5H)	–	–
3i	1.0	29	130°	$C_{14}H_{18}O_3Si$ (262.4)	262.1022[g] (262.1023)	1.1 (t, 2H, *J* = 9 Hz); 1.76 (d, 3H, *J* = 13 Hz); 2.64 (d, 3H, *J* = 13 Hz); 2.75 (t, 2H, *J* = 9 Hz); 4.52 (br. s, 3H); 7.13 (s, 5H)	–	–
3j	1.0	10	76°	$C_{14}H_{18}O_3Si$ (262.4)	262.1020[g] (262.1023)	1.37 (d, 3H, *J* = 8 Hz); 1.65 (d, 3H, *J* = 14 Hz); 2.26 (q, 1H, *J* = 8 Hz); 2.53 (t, 3H, *J* = 14 Hz); 4.83 (br. s, 3H); 7.2–7.4 (m, 5H)	–	–
3k	1.5	56[j]	oil	$C_{14}H_{26}O_3Si$ (270.5)	270.1648[g] (270.1649)	0.5–1.4 (m, 17H); 1.68 (d, 3H, *J* = 14 Hz); 2.79 (d, 3H, *J* = 14 Hz); 4.25 (br. s, 3H)	–	–
3l	1.1	33	64°[f]	$C_{12}H_{20}O_3Si$ (240.4)	240.1176[g] (240.1181)	0.7–1.9 (m, 14H); 2.52 (d, 3H, *J* = 14 Hz); 4.48 (br. s, 3H)	–	–
3m	2.0	52	65°[f]	$C_{15}H_{20}O_4Si$ (292.4)	292.1129[g] (292.1129)	0.83 (t, 2H, *J* = 7 Hz); 1.70 (d, 3H, *J* = 12 Hz); 2.52 (q, 2H, *J* = 7 Hz); 2.84 (d, 3H, *J* = 12 Hz); 3.87 (t, 2H, *J* = 7 Hz); 4.38 (br. s, 3H); 6.5–7.2 (m, 5H)	–	–

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[a] All reactions were carried out in benzene for 15–18 h at reflux in the presence of tris(triphenylphosphine)rhodium(I) chloride (0.4–0.7 mol%) unless otherwise stated.

[b] Hydrogen hexachloroplatinate (IV) (0.1 mol%) was used as catalyst in dichloromethane at reflux for 70 h.

[c] After sublimation.

[d] Bis(triphenylphosphine)platinum(II) chloride (0.5%) was used as catalyst.

[e] Determined by G.L.C.

[f] Decomposition.

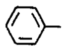
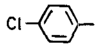
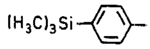
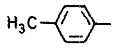
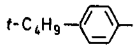
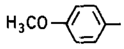
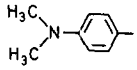
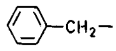
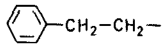
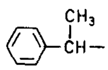
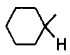
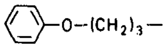
[g] Reproducible microanalyses were not obtained because of the instability of the products. Molecular formula was confirmed by high resolution MS.

[h] Satisfactory microanalyses obtained: C ±0.22, H ±0.3.

[i] Recrystallized from *n*-hexane after sublimation.

[j] After molecular distillation.

Table 2. Trihydrosilanes **1** prepared

Product No.[a]	R	Yield [%]	b.p. [°C]/torr	Molecular formula[b] or Lit. b.p. [°C]/torr	M.S. *m/e* (relative intensity, %)	^{1}H-N.M.R. (CCl_4) δ [ppm]
1a		84	118°	120°/760^{16}	108 (M^+, 100); 107 (98)	4.27 (s, 3H); 7.2–7.4 (m, 5H)
1b		84	99°/121	65–66.5°/30^{18}	142 (M^+, 60); 63 (100)	4.26 (s, 3H); 7.31 (d, 2H, $J = 8$ Hz); 7.52 (d, 2H, $J = 8$ Hz)
1c		64	80°/13	$C_9H_{10}Si_2$ (174.4)	180 (M^+, 14); 165 (100)	0.33 (s, 9H); 4.24 (s, 3H); 7.4–7.6 (m, 4H)
1d		83	146°	147–148°/760^{19}	122 (M^+, 75); 91 (100)	2.32 (s, 3H); 4.04 (s, 3H); 7.09 (d, 2H, $J = 7$ Hz); 7.48 (d, 2H, $J = 7$ Hz)
1e		77	78°/15	$C_{10}H_{16}Si$ (164.3)	164 (M^+, 26); 149 (100)	1.4 (s, 9H); 4.25 (s, 3H); 7.3–7.6 (m, 4H)
1f		69	84–86°/45	75–76°/21^{20}	138 (M^+, 76); 59 (100)	3.77 (s, 3H); 4.2 (s, 3H); 6.8 (d, 2H, $J = 9$ Hz); 7.43 (d, 2H, $J = 9$ Hz)
1g		68	106–108°/15	81°/5^{21}	151 (M^+, 100); 121 (97)	2.85 (s, 6H); 4.12 (s, 3H); 6.48 (d, 2H, $J = 8$ Hz); 7.27 (d, 2H, $J = 8$ Hz)
1h		66	48–49°/50	84°/93^{22}	–	2.22 (q, 2H, $J = 4$ Hz); 3.7 (t, 3H, $J = 4$ Hz); 6.9–7.4 (m, 5H)
1i[c]		27	77–79°/20[d]	163.8°/743^{23}	–	0.8–1.3 (m, 2H); 2.6–2.9 (m, 2H); 3.36 (t, 3H, $J = 8$ Hz); 7.0–7.3 (m, 5H)
1j[c]		–	–	171.5°/743^{23}	–	1.45 (d, 3H, J = 8 Hz); 2.2–2.4 (m, 1H); 3.65 (d, 3H, $J = 4$ Hz); 7.0–7.5 (m, 5H)
1k	*n*-C_8H_{17}	84	60°/10	61°/20^{24}	–	0.4–1.6 (m, 17H); 3.47 (t, 3H, $J = 4$ Hz)
1l		77	94°	119.5°/739.5^{20}	–	1.0–1.9 (m, 11H); 3.36 (d, 3H, $J = 4$ Hz)
1m		27[e]	51–52°/0.9	$C_9H_{14}OSi$[f] (166.3)	166 (M^+, 57); 94 (100)	0.7–1.1 (m, 2H); 1.7–2.1 (m, 2H); 3.57 (t, 3H, $J = 4$ Hz); 3.87 (t, 2H, $J = 6$ Hz); 6.6–7.3 (m, 5H)

[a] All compounds show a characteristic band in I.R. spectra due to ν_{Si-H} around 2160 cm^{-1}.

[b] Satisfactory microanalyses obtained: C ±0.4, H ±0.14

[c] **1i** and **1j** were isolated by preparative G.L.C.

[d] B.p. of a mixture of **1i** and **1j**.

[e] Overall yield of hydrosilylation followed by reduction with lithium aluminium hydride.

[f] High resolution M.S.: *m/e* of $M^+ = 166.0812$ (calc. 166.0813).

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