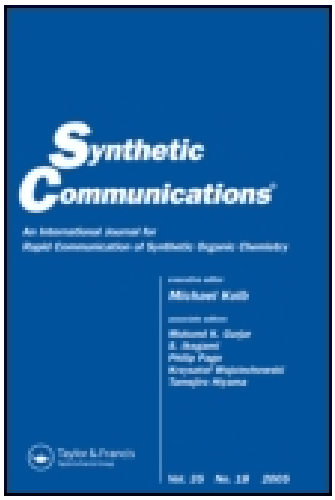

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SYNTHESIS OF γ-N-ARYLIDENEAMINOPROPYL-2-METHYL-6-PHENYL-1,3-DIOXA-6-AZA-2-SILACYCLOOCTANES

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SYNTHESIS OF γ-*N*-ARYLIDENEAMINOPROPYL-2-METHYL-6-PHENYL-1,3-DIOXA-6-AZA-2-SILACYCLOOCTANES

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ABSTRACT

Several new γ-*N*-arylideneaminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctanes have been prepared by the reaction of γ-aminopropyldimethoxymethylsilane with phenyldiethanolamine first and then with arylaldehydes. The products were identified by elemental analyses, IR and ^{1}H NMR.

Silatranes[1,2] containing Schiff's base component (Figure 1) have been synthesized and studied.[3–5] It has been reported that some of them show definite antitumor activity.[3,4] In those compounds, the main groups, are the pentacoordinate bond as a result of transannular dative bonding between

* Corresponding author.

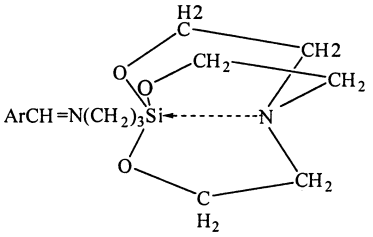
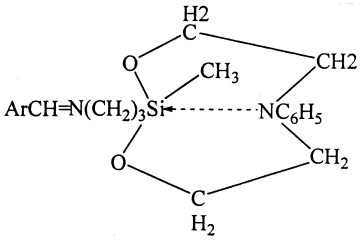


Figure 1.

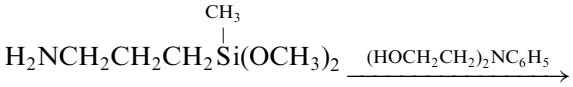


III

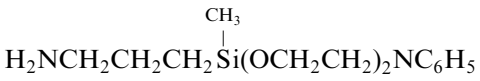
Figure 2.

the nitrogen and silicon atoms[1] and the Schiff's base component. To study further those structures and their analogies, several new pseudosilatranes[6] (III in Figure 2) which contain Schiff's base component and an eight member heterocycle bridged by weak nitrogen-silicon interaction,[7,8] have been prepared by the condensation of arylaldehydes with 3-aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane **II**.

Our synthesis started with an alcohol exchange reaction on silane **I** with phenyldiethanolamine (Scheme 1). In the first step, the principal side reaction is the polymerization. In order to obtain a good yield, a solvent/reactant ratio of 2:1 was used.



I



II

Scheme 1.

The final products were synthesized as depicted in Scheme 2. In this step anhydrous K_2CO_3 was used as desiccant and dry benzene as solvent. Residual water was removed by azeotropic distillation.

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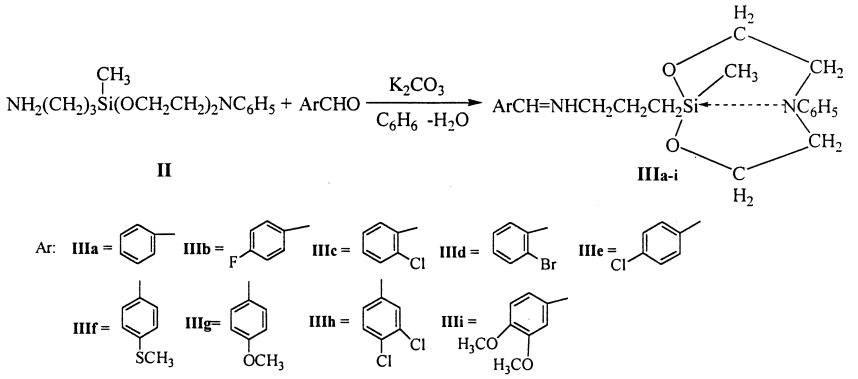

Scheme 2.

The results are listed in the Table.

Table. Reaction Time, Yield, and Physicochemical Data

Entry	Ar	Physical Data	Reaction Time (h) (R.T.) (for scheme 2)	Reaction Yield	
				Scheme 2	Total Reaction
IIIa	C_6H_5	Light yellow (oil)	3 h	99%	80%
IIIb	*p*-C_6H_4F	Light yellow (oil)	2 h	99%	80%
IIIc	*o*-C_6H_4Cl	Yellow	2 h	99%	80%
IIId	*o*-C_6H_4Br	Yellow (oil)	2 h	99%	80%
IIIe	*p*-C_6H_4Cl	Light yellow (oil)	2 h	99%	80%
IIIf	*p*-$C_6H_4SCH_3$	Light yellow (oil)	6 h	98%	79%
IIIg	*p*-$C_6H_4OCH_3$	Yellow (oil)	10 h	99%	80%
IIIh	*m,p*-$C_6H_3Cl_2$	Light yellow (oil)	2 h	99%	80%
IIIi	*m,p*-$C_6H_3(OCH_3)_2$	Yellow (oil)	12 h	98%	79%

EXPERIMENTAL

IR spectra were recorded with VECTOR 22 IR spectrometer in the region 4000–400 cm^{-1}. Proton nuclear resonance spectra were obtained on a FX90Q spectrometer using $CDCl_3$ as solvent. Elemental analyses were carried out on a Yanaco MT-3 elemental analyzer. Thermometers were not corrected.

Synthesis of γ-Aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane(II)

To a 500 mL dry flask, 35.05 g (0.218 mol) I (distilled in 184–187°C), 39.45 g (0.218 mol) phenyldiethanolamine and 250 mL toluene were added. The mixture was refluxed for 8 h. The reaction product about 12.5 g methanol was distilled off. The mixture was heated for another 10 h at 100°C. Toluene was removed and the crude product was distilled *in vacuum* to give 49.90 g III. b.p 188–190°C/10 mmHg; yield: 81%. IR (cm^{-1}): 3370, 3022, 3058, 2920, 2877, 1134, 1067, 537, 505; ^{1}H NMR ($CDCl_3$): δ (ppm): 0.05 (3H, s; CH_3-Si), 0.58(2H, t; CH_2-Si), 1.55 (4H, m; CH_2-C-Si, H_2N), 2.68 (2H, t; CH_2-C-C-Si), 3.75 (4H, m; CH_2-N), 4.07 (4H, t; CH_2-O), 6.70–7.45 (5H, m; Ar-H); Anal. Calcd (%). for $C_{14}H_{24}N_2O_2Si$: C 59.96, H 8.63, N 9.99, Found (%): C 59.87, H 8.59, N 9.84.

Synthesis of γ-*N*-Arylideneaminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctanes(IIIa–i)

General Procedure (Using IIIb as Example)

All aryl aldehydes were distilled *in vacuum* prior to use.

Into a dried 25 mL round bottomed flask, 2.321 g (8.29 mmol), **II**, 1.03 g (8.29 mmol) 4-fluorobenaldehyde, 15 mL dry benzene and 2 g of K_2CO_3 were added. The mixture was shaken and then allowed to stand at room temperature for over 2 h. K_2CO_3 was filtered off. The flask was fitted with 20 cm Vigreux column and the benzene was distilled slowly. Additional benzene was added continuously to keep about 10 mL solvent in the flask for 1 h. The solvent was distilled first under normal pressure and then in vacuum (110°C/5–10 mmHg) for 3 h to obtain product **IIIb**: 3.32 g Yield: 99%.

IIIa–i were prepared by the similar procedure. The chemical name, IR, ^{1}H NMR, and elemental analyses data are listed below.

γ-*N*-Benzylideneaminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIa): IR (cm^{-1}): 3025, 3058, 1645, 1136, 1069, 534, 505; ^{1}HNMR ($CDCl_3$): δ (ppm): −0.04 (3H, s; CH_3-Si), 0.54 (2H, t; CH_2-Si), 1.75 (2H, m; CH_2-C-Si), 3.52 (6H, m; CH_2N), 3.88 (4H, t; CH_2-O), 6.70–7.45 (10H, m; Ar-H), 8.08 (1H, s; CH=N); Anal. Calcd (%). for $C_{21}H_{28}N_2O_2Si$: C 68.44, H 7.66, N 7.60, Found (%): C 68.15, H 7.55, N 7.73.

γ-*N*-(*p*-Fluorobenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIb): IR (cm^{-1}): 3062, 3039, 1648, 1136, 1069, 535, 505; ^{1}H NMR ($CDCl_3$): δ (ppm): 0.01 (3H, s; CH_3-Si), 0.64 (2H, t; CH_2-Si), 1.79

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(2H, m; CH_2-C-Si), 3.55 (6H, m; CH_2N), 4.01 (4H, t; CH_2-O), 6.69–7.81 (9H, m; Ar-H), 8.17 (1H, s; CH=N); Anal. Calcd (%). for $C_{21}H_{27}N_2O_2SiF$: C 65.25, H 7.04, N 7.25, Found (%): C 65.60, H 7.03, N 7.43.

γ-*N*-(*o*-Chlorobenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIc): IR (cm^{-1}): 3063, 3025, 1637, 1137, 1069, 535, 505; ^{1}HNMR ($CDCl_3$): δ (ppm): −0.05 (3H, s; CH_3-Si), 0.56 (2H, t; CH_2-Si), 1.75 (2H, m; CH_2-C-Si), 3.55 (6H, m; CH_2N), 3.95 (4H, t; CH_2-O), 6.57–7.98 (9H, m; Ar-H), 8.53 (1H, s; CH=N); Anal. Calcd (%) for $C_{21}H_{27}N_2O_2SiCl$: C 62.59, H 6.75, N 6.95, Found (%): C 62.35, H 6.55, N 6.89.

γ-*N*-(*o*-Brombenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIId): IR (cm^{-1}): 3062, 3024, 1635, 1137, 1069, 535, 505; ^{1}H NMR ($CDCl_3$): δ (ppm): −0.06 (3H, s; CH_3-Si), 0.54 (2H, t; CH_2-Si), 1.74 (2H, m; CH_2-C-Si), 3.55 (6H, m; CH_2N), 3.95 (4H, t; CH_2-O), 6.57–8.02 (9H, m; Ar-H), 8.55 (1H, s; CH=N); Anal. Calcd (%). for $C_{21}H_{27}N_2O_2SiBr$: C 56.37, H 6.08, N 6.26, Found (%): C 56.37, H 6.33, N 6.16.

γ-*N*-(*p*-Chlorobenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIe) : IR (cm^{-1}): 3062, 3024, 1645, 1137, 1069, 537, 505; ^{1}H NMR ($CDCl_3$): δ (ppm): −0.01 (3H, s; CH_3-Si), 0.49 (2H, t; CH_2-Si), 1.61 (2H, m; CH_2-C-Si), 3.46 (6H, m; CH_2N), 3.88 (4H, t; CH_2-O), 6.50–7.55 (9H, m; Ar-H), 8.00 (1H, s; CH=N); Anal. Calcd (%). for $C_{21}H_{27}N_2O_2SiCl$: C 62.59, H 6.75, N 6.95, Found (%): C 62.42, H 6.85, N 7.08.

γ-*N*-(*p*-Methylthiobenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIf): IR (cm^{-1}): 3023, 1641, 1135, 1069, 536, 506; ^{1}H NMR ($CDCl_3$): δ (ppm): −0.06 (3H, s; CH_3-Si), 0.51 (2H, t; CH_2-Si), 1.71 (2H, m; CH_2-C-Si), 2.48 (3H, S:CH_3S), 3.56 (6H, m; CH_2N), 3.94 (4H, t; CH_2-O), 6.57–7.65 (9H, m; Ar-H), 8.09 (1H, s; CH=N); Anal. Calcd (%). for $C_{22}H_{30}N_2O_2SSi$: C 63.73, H 7.29, N 6.76, Found (%): C 63.58, H 7.01, N 6.86.

γ-*N*-(*p*-Methoxybenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctanes (IIIg): IR (cm^{-1}): 3062, 1637, 1137, 1069, 536, 505; ^{1}H NMR ($CDCl_3$): δ (ppm): −0.03 (3H, s; CH_3-Si), 0.56 (2H, t; CH_2-Si), 1.75 (2H, m; CH_2-C-Si), 3.55 (9H, m; CH_3O, CH_2N), 3.93 (4H, t; CH_2-O), 6.59–7.98 (9H, m; Ar-H), 8.65 (1H, s; CH=N); Anal. Calcd (%). for $C_{22}H_{30}N_2O_3Si$: C 66.30, H 7.59, N 7.03, Found (%): C 66.30, H 7.59, N 7.13.

γ-*N*-(*m,p*-Dichlorobenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIh): IR (cm^{-1}): 3062, 1647, 1137, 1069, 536, 505; ^{1}H NMR ($CDCl_3$): δ (ppm): −0.01 (3H, s; CH_3-Si), 0.55 (2H, t; CH_2-Si), 1.77 (2H, m; CH_2-C-Si), 3.55 (6H, m; CH_2N), 3.99 (4H, t; CH_2-O), 6.61–7.83 (8H, m; Ar-H), 8.08 (1H, s; CH=N); Anal. Calcd (%). for

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$C_{21}H_{26}N_2O_2SiCl_2$: C 57.66, H 5.99, N 6.40. Found (%): C 57.55, H 6.40, N 6.39.

γ-*N*-(*m*,*p*-Dimethoxybenzylidene)aminopropyl-2-methyl-6-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (IIIi): IR (cm^{-1}): 3061, 1644, 1135, 1069, 536, 505; ^1H NMR ($CDCl_3$): δ (ppm): 0.03 (3H, s; CH_3-Si), 0.60 (2H, t; CH_2-Si), 1.70 (2H, m; CH_2-C-Si), 3.61-3.72 (12H, S: CH_3O, CH_2N), 4.01 (4H, t; CH_2-O), 6.66–7.49 (8H, m; Ar-H), 8.16 (1H, s; CH=N); Anal. Calcd (%). for $C_{23}H_{32}N_2O_4Si$: C 64.45, H 7.52, N 6.55, Found (%): C 64.45, H 7.42, N 6.41.

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