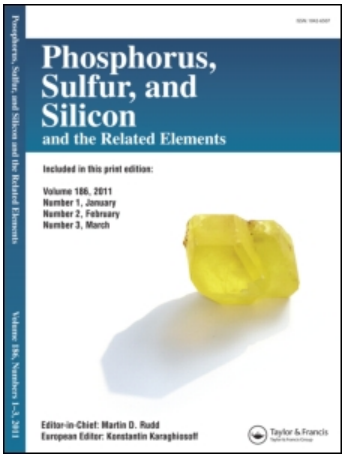

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SYNTHESIS OF 1-(O,O-DIALKYLPHOSPHORYL-AMIDO)PROPYL-5-AZA-2,8,9-TRIOXA-1-SILATRICYCLO-[3,3,3,$0^{1,5}$] UNDECANES

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Ten 1-(O,O-dialkyl phosphorylamido)propyl-5-aza-2,8,9-trioxa-1-silatricyclo [3,3,3,$0^{1,5}$] undecanes were synthesized by the reaction of dialkoxy phosphoryl chlorides with aminopropyl silatrane and their structures were established by elemental analysis, IR, ^{1}HNMR, and MS measurement. The suitable reaction conditions are discussed based on the related reaction mechanism.

Keywords: Organosilicon compound; phosphoroamide; silatrane

1-Organyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecanes, so-called silatranes, have obvious physiological activities and their biological activity greatly related to the substituents on silicon atom. 1-Arylsilatrane, for example, was highly toxic material and used as rodenticide,[1] while 1-alkyl or 1-alkoxysilatranes were physiologically indolent,[2] some of them even used in medical to heal the wounds or stimulate hair-growth.[3,4] It was well known that phosphonates possessed outstanding biological activities and were widely used as medicine and agricultural chemicals.[5–7] Supposing the silatrane skeleton combined with phosphonate in a single molecule, their individual biological activity may increase or even arise some new activities. On the basis of the idea, ten silatranes containing phosphonate were synthesized by the reaction of aminopropylsilatrane with dialkoylphosphoryl chloride and their structures were established by IR, ^{1}HNMR, MS and elemental analysis, the reaction is show in Scheme 1.

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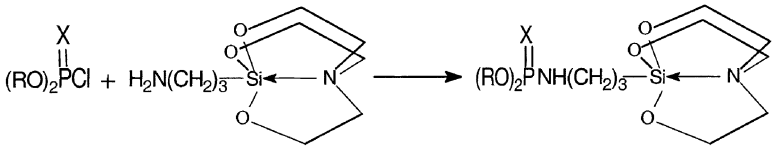
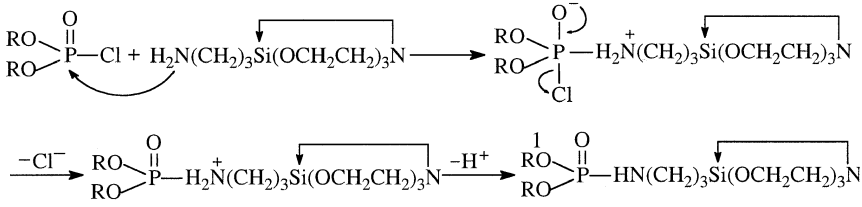


X=O: **1**. R=Me; **2**. R=Et; **3**. R=n-Pr; **4**. R=i-Pr; **5**. R=n-Bu;
X=S: **6**. R=Me; **7**. R=Et; **8**. R=n-Pr; **9**. R=i-Pr; **10**. R=n-Bu.

SCHEME 1

RESULTS AND DISCUSSIONS

The reaction is functional group transformation on the side chain of silatrane, which belongs to nucleophilic addition-elimination. The amino group first attacks on the phosphorus atom forming betaine intermediate that then lose hydrogen chloride and produce the target compound. The reaction mechanism may be described as shown in Scheme 2.



SCHEME 2

The steric effect of silatrane made the nucleophilic approach more difficult than that of normal amines,[8] therefore, the careful choice of reaction condition was very important. Ethyl acetate was selected as reaction medium through experiments and the mixture was heated to reflux to ensure completion of the reaction. To avoid the hydrogen chloride generated during the reaction cause the silatrane ring cleavage and further polymerization,[9] the presence of a tertiary amine as scavenger of hydrogen chloride is necessary.

In their IR spectra, the target compounds have an approximate symmetry of C_3V for the main cyclic silatrane skeleton. It was know that the IR absorption spectra of compounds with Si—O—C grouping[10] present a very intense band at 1100 cm^{-1} and bands of variable intensity in the interval of 620–840 cm^{-1}. The frequency near 1100 cm^{-1} was assigned to the unsymmetric C—O bond prevailing; frequency of the region 800–840 cm^{-1} were attributed to symmetric stretching vibration of Si—O

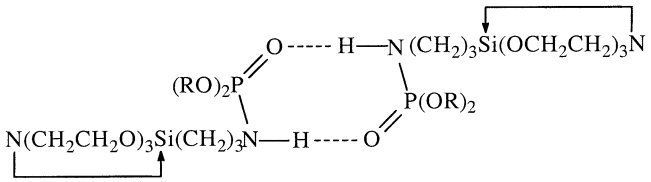


FIGURE 1 Intermolecular hydrogen bond.

bond. The vibration frequency of N—H in 3276~3289 cm^{-1} seems a little lower than that of the normal N—H bond,[11] the reason may owe partly to the intermolecular hydrogen bond forming with P=O group.

The participation of the unshared nitrogen electron pair with the silicon atom achieved through its vacant 3d-orbital to form a transannular dipole coordinate Si ← N bond. This peculiar electronic trait of the silatrane molecules could be easily observed in their IR and NMR spectra.[12] The frequency of the coordinate Si ← N bond in silatranes at about 585 cm^{-1} was lower than that of the ordinary Si—N bond.[13]

The NMR spectrum of $-OCH_2-CH_2N-$ fragment in silatrane molecules reflects the A_2X_2 system expressed in small constant values of the spin-spin interaction between CH_2 and CH_2 protons (5–6 Hz), the Si ← N bond formation led to an increase in electron density at the silicon atom but the nitrogen atom lost some electron density. A certain asymmetry of the two triplets is due to the fact that the A_2X_2 system is not clearly expressed and tends toward A_2B_2.

EXPERIMENTAL

IR spectra were measured on a Perkin Elmer-983 spectrophotometer (KBr), ^{1}HNMR spectra were recorded on a Varian Associates XL-200 instrument, chemical shifts are reported in ppm on the δ scale relative to a tetramethylsilane internal standard, MS were recorded on a HP5988A mass spectrometer. Elemental analyses were performed on a Perkin Elmer-2400 automatic meter. Temperatures were uncorrected.

1-aminopropyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane was prepared by the reaction of triethanolamine and aminopropyl triethoxysilane.[14] Dialkylphosphoryl chloride was prepared based on the method described by literature.[15]

1-(O,O-dimethyl phosphoryl amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**1**). To a mixture of 1-aminopropyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecanes (2.32 g, 10 mmol),

triethanolamine (1.06 g, 10 mmol) and 20 ml ethyl acetate, a solution of dimethylphosphoryl chloride (1.5 g, 10 mmol) in 10 ml ethyl acetated was added within 30 min, stirred for 5 h at room temperature until reaction material disappeared by Thin Layer Chromatograghy detection. Filtrated, washed with water and ethyl acetate respectively, then recrystallized from anhydrous ethanol to afford **1** (70%), m.p. 116–118°C. IR: 3285 (N—H), 1275 (P=O), 1188 (P—O—C), 1010 (Si—O), 942 (P—N), 585 (Si ← N). ^{1}HNMR: 0.4(t, 2H, —CH_2Si), 1.56 (m, 2H, —C$\underline{H}_2CH_2$Si), 2.8 (m, 8H, NHC$\underline{H}_2$, 3 × NCH_2—), 3.24 (s, 6H, 2 × CH_3O), 3.78∼4.00 (m, 7H, NH, SiOCH_2). Anal. Calcd for $C_{11}H_{25}N_2O_6PSi$ (340): C, 38.82; H, 7.35; N, 8.21. Found: C, 38.70; H, 7.22; N, 8.30.

1-(O,O-diethyl phosphoryl amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**2**). Yield (75%), m.p. 112–113°C. IR: 3286 (N—H), 1273 (P=O), 1186 (P—O—C), 1010 (Si—O), 942 (P—N), 585 (Si ← N). ^{1}HNMR: 0.4 (t, 2H, —CH_2Si), 1.30 (t, 6H, 2 × CH_3), 1.56 (m, 2H, —C$\underline{H}_2CH_2$Si), 2.8 (m, 8H, NHC$\underline{H}_2$, 3 × NCH_2—), 3.24 (q, 4H, —CH_2O), 3.78∼4.00 (m, 7H, NH, SiOCH_2). MS: m/e (%) = 368 (M^+, 2.5), 130 (100). Anal. Calcd for $C_{13}H_{29}N_2O_6PSi$ (368): C, 42.39; H, 7.88; N, 7.60. Found: C, 42.42; H, 7.78; N, 7.70.

1-(O,O-dipropyl phosphoryl amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**3**). Yield (48%), m.p. 134–135°C. IR: 3278 (N—H), 1276 (P=O), 1188 (P—O—C), 1010 (Si—O), 942 (P—N), 583 (Si ← N). ^{1}HNMR: 0.42 (t, 2H, —CH_2Si), 0.96 (t, —6H, 2 × CH_3), 1.32–1.58 (m, 6H), 2.8 (m, 8H, NHC$\underline{H}_2$, 3 × NCH_2—), 3.70∼4.02 (m, 11H, NH, —CH_2O, SiOCH_2). Anal. Calcd for $C_{15}H_{33}N_2O_6PSi$ (396): C, 45.45; H, 8.35; N, 7.07. Found: C, 45.51; H, 8.42; N, 7.13.

1-(O,O-disopropyl phosphoryl amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**4**). Yield (67%), m.p. 96–98°C. IR: 3280 (N—H), 1373 (P=O), 1188 (P—O—C), 1010 (Si—O), 942 (P—N), 585 (Si ← N). ^{1}HNMR: 0.41 (t, 2H, —CH_2Si). 1.18 (d, 12H, 4 × CH_3), 1.56 (m, 2H, —C$\underline{H}_2CH_2$Si), 2.8 (m, 8H, NHC$\underline{H}_2$, 3 × NCH_2—), 3.78∼4.03 (m, 9H, NH, —CHO, SiOCH_2). Anal. Calcd for $C_{15}H_{33}N_2O_6PSi$ (396): C, 45.45; H, 8.35; N, 7.07. Found: C, 45.52; H, 8.32; N, 7.15.

1-(O,O-dibutyl phosphoryl amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**5**). Yield (40%), m.p. 142–144°C. IR: 3277 (N—H), 1279 (P=O), 1188 (P—O—C), 1010 (Si—O), 942 (P—N), 584 (Si ← N). ^{1}HNMR: 0.4 (t, 2H, —CH_2Si), 0.83 (t, —6H, 2 × CH_3), 1.26–1.64 (m, 10H), 2.8 (m, 8H, NHC$\underline{H}_2$, 3 × NCH_2—), 3.68–3.96 (m, 11H, NH, SiOCH_2). Anal. Calcd for $C_{17}H_{37}N_2O_6PSi$ (424): C, 48.11; H, 8.73; N, 6.60. Found: C, 48.20; H, 8.52; N, 6.63.

1-(O,O-dimethyl phosphorothioate amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**6**). Yield (73%), m.p. 114–115°C. IR: 3289 (N—H), 769 (P=S), 1186 (P—O—C), 1010 (Si—O), 942 (P—N), 583

(Si ← N). ^{1}HNMR: 0.43 (t, 2H, —CH_2Si), 1.55–1.62 (m, 2H, —C$\underline{H_2}CH_2$Si), 2.8 (m, 8H, NHC$\underline{H_2}$, 3 × NCH_2—), 3.68(s, 6H, 2 × CH_3O), 3.72∼3.78 (m, 7H, NH, $SiOCH_2$). Anal. Calcd for $C_{11}H_{25}N_2O_5PSSi$ (356): C, 37.08; H, 7.02; N, 7.87. Found: C, 36.94; H, 7.24; N, 7.90.

1-(O,O-diethyl phosphorothioate amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**7**). Yield (82%), m.p. 117–118°C. IR: 3286 (N—H), 761 (P═S), 1186 (P—O—C), 1010 (Si—O), 942 (P—N), 582 (Si ← N). ^{1}HNMR: 0.4 (t, 2H, —CH_2Si), 1.30 (t, —6H, 2 × CH_3), 1.56 (m, 2H, —C$\underline{H_2}CH_2$Si), 2.8 (m, 8H, NHC$\underline{H_2}$, 3 × NCH_2—), 3.24 (q, 4H, —CH_2O), 3.78∼4.00 (m, 7H, NH, $SiOCH_2$). Anal. Calcd for $C_{13}H_{29}N_2O_5PSSi$ (384): C, 40.63; H, 7.55; N, 7.29. Found: C, 40.82; H, 7.40; N, 7.35.

1-(O,O-dipropyl phosphorothioate amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**8**). Yield (72%), m.p. 135–137°C. IR: 3278 (N—H), 765 (P═S), 1186 (P—O—C), 1010 (Si—O), 942 (P—N), 584 (Si←N). ^{1}HNMR: 0.4 (t, 2H, —CH_2Si), 1.30 (t, —6H, 2 × CH_3), 1.56 (m, 2H, —C$\underline{H_2}CH_2$Si), 2.8 (m, 8H, NHC$\underline{H_2}$, 3 × NCH_2—), 3.24 (q, 4H, —CH_2O), 3.78∼4.00 (m, 7H, NH, $SiOCH_2$). Anal. Calcd for $C_{15}H_{33}N_2O_5PSSi$ (412): C, 43.69; H, 8.01; N, 6.80. Found: C, 43.78; H, 7.78; N, 6.59.

1-(O,O-diisopropyl phosphorothioate amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo [3,3,3,$0^{1,5}$] undecane (**9**). Yield (65%), m.p. 179–181°C. IR: 3281 (N—H), 764 (P═S), 1186 (P—O—C), 1010 (Si—O), 942 (P—N), 584 (Si ← N). ^{1}HNMR: 0.4 (t, 2H, —CH_2Si), 1.30 (t, —6H, 2 × CH_3), 1.56 (m, 2H, —C$\underline{H_2}CH_2$Si), 2.8 (m, 8H, NHC$\underline{H_2}$, 3 × NCH_2—), 3.24 (q, 4H, —CH_2O), 3.78 ∼ 4.00 (m, 7H, NH, $SiOCH_2$). Anal. Calcd for $C_{15}H_{33}N_2O_5PSSi$ (412): C, 43.69; H, 8.01; N, 6.80. Found: C, 43.42; H, 8.12; N, 6.94.

1-(O,O-dibutyl phosphorothioate amido) propyl-5-aza-2,8,9-trioxa-1-silatricyclo[3,3,3,$0^{1,5}$] undecane (**10**). Yield (60%), m.p. 175–177°C. IR: 3280 (N—H), 760 (P═S), 1186 (P—O—C), 1010 (Si—O), 942 (P—N), 585 (Si ← N). ^{1}HNMR: 0.4 (t, 2H, —CH_2Si), 1.30 (t, —6H, 2 × CH_3), 1.56 (m, 2H, —C$\underline{H_2}CH_2$Si), 2.8 (m, 8H, NHC$\underline{H_2}$, 3 × NCH_2—), 3.24 (q, 4H, —CH_2O), 3.78∼4.00 (m, 7H, NH, $SiOCH_2$). Anal. Calcd for $C_{17}H_{37}N_2O_5PSSi$ (440): C, 46.36; H, 8.41; N, 6.36. Found: C, 46.71; H, 8.28; N, 6.52.

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