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Novel silicon-bridged macrocycles: efficient synthesis by quadruple cycloadditive macrocyclization and intramolecular nitrile oxide dimerization

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Abstract

Novel silacyclophanes have been synthesized by using quadruple cycloadditive macrocyclization and intramolecular nitrile oxide dimerization. The macrocyclic cycloadducts were characterized by spectroscopic methods and X-ray crystallography. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: macrocycles; silicon heterocycles; cycloadditions; nitrile oxides.

Silicon-bridged macrocycles are of interest due to their additional coordination sites compared to carbomacrocycles and good chemophysical properties including solubility. So far synthetic efforts toward silacalixarenes,[1] silacyclophanes,[2] and a silacrown[3] have been reported. We report here the facile synthesis of novel silacyclophanes by using the quadruple cycloadditive macrocyclization (QCM) methodology[4] and intramolecular nitrile oxide dimerization,[5] and their X-ray crystal structures. QCM methodology based on 1,3-dipolar cycloaddition reaction provides a very efficient way to the silamacrocycles due to the short reaction sequences.

Silamacrocycle **3** was synthesized in a two-step sequence by using QCM methodology (Scheme 1).[4] Double cycloadditions between in situ-generated isophthaldinitrile oxide and 1,3-divinyltetramethyldisiloxane provided [1+2] cycloadduct **2** as the major intermediate and further cycloadditions between **2** and isophthaldinitrile oxide afforded the final [2+2] cycloadduct **3**[6] as the major product in 25% overall yield. The structure of silacyclophane **3** was identified by elemental analysis, mass spectroscopy, IR, ^{1}H NMR and ^{13}C NMR, and confirmed by X-ray crystallography (Fig. 1).[7] The relative stereochemistry of the intermediate **2** was tentatively assigned by the X-ray crystal structure of the final product **3**. In a similar fashion, silacyclophanes **6**[6] was prepared by QCM methodology between terephthaldinitrile oxide and 1,3-divinyltetramethyldisiloxane (Scheme 1). Thus,

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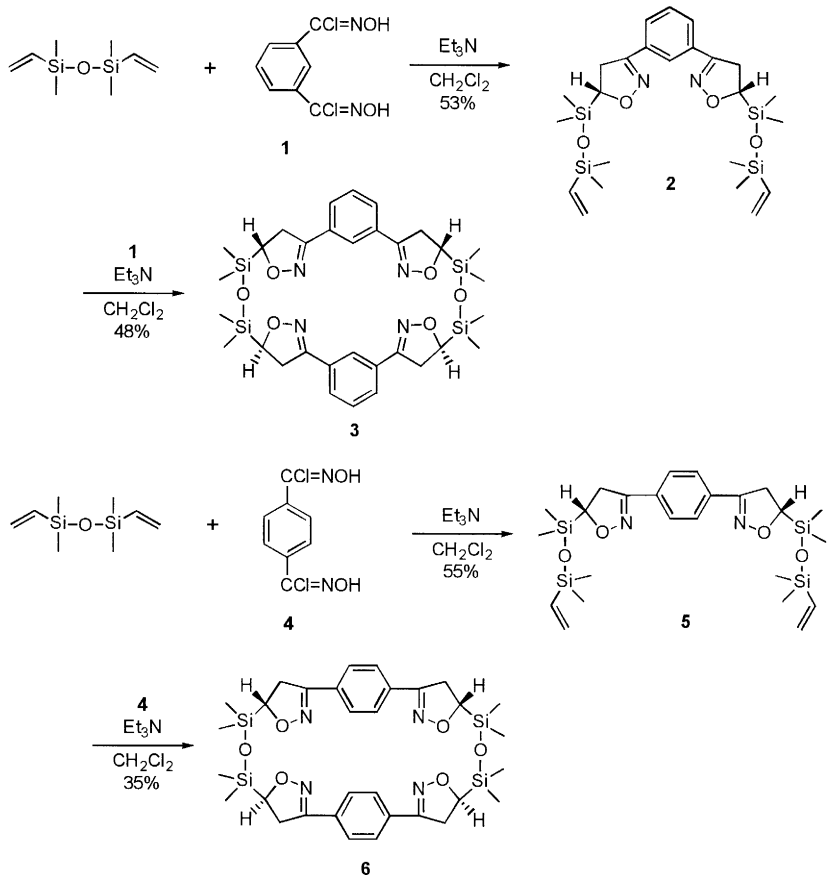
1,3-divinyltetramethyldisiloxane was served well as a bifunctional siladipolarophile with benzene-based bifunctional dipoles.



Scheme 1.

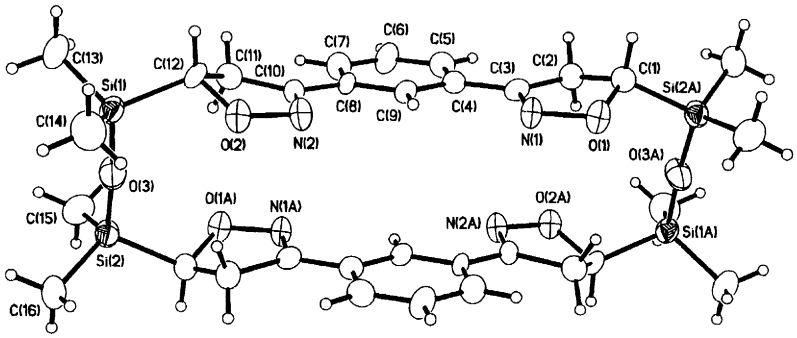
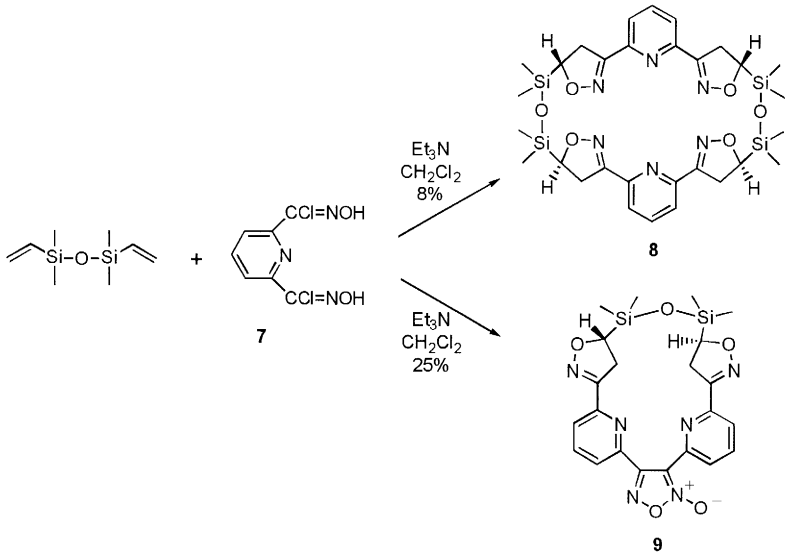


Fig. 1. X-Ray crystal structure of **3**

In the case of QCM with 2,6-pyridinedintrile oxide, two macrocyclic cycloadducts were isolated. The first was the regular [2+2] cycloadduct **8**[6] (8%) and the second was a [2+1] triple cycloadduct **9**[6] (25%) (Scheme 2). Silamacrocycle **8** is the pyridine version of compound **3** and was formed through QCM in one pot. However, formation of compound **9** is rather unique and deserves attention. Very recently, Mioskowski and co-workers[5] reported the synthesis of medium- and large-size rings by intramolecular

nitrile oxide dimerization, which results in the formation of furoxan moiety. During the dimerization process, one of the nitrile oxides acts as a dipole whereas the other acts as a dipolarophile. Formation of compound **9** proceeds via [2+1] double cycloadditions followed by intramolecular nitrile oxide dimerization. Generation of the rather unusual product **9** may be attributable to the stability of 2,6-pyridinedinitrile oxide and the proximity between two nitrile oxide moieties. The chemical structure of **9** was confirmed by X-ray crystallography (Fig. 2).[7]



Scheme 2.

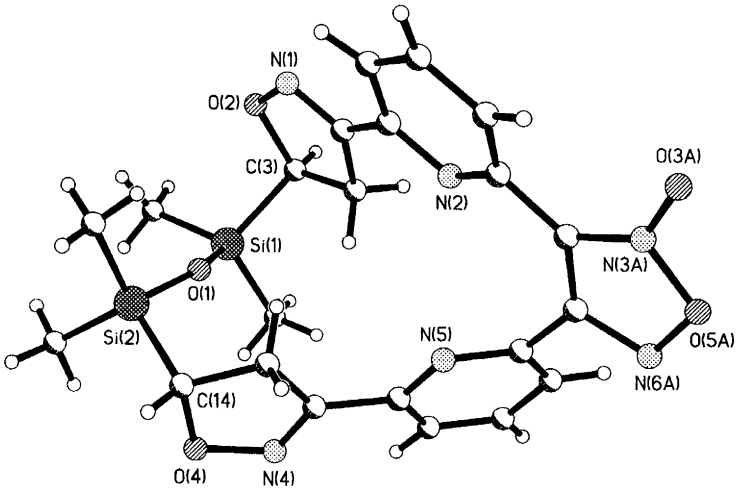


Fig. 2. X-Ray crystal structure of **9**

In summary, we have synthesized novel silacyclophanes by using quadruple cycloadditive macrocyclization and intramolecular nitrile oxide dimerization. With suitable siladipolarophiles these methodologies will provide an efficient route to various silamacrocycles.

Acknowledgements

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6. Selected spectroscopic data of **3**, **6**, **8** and **9**. Compound **3**: mp 267–270°C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.77 (s, 2H, ArH), 7.60 (d, 4H, *J*=7.8 Hz, ArH), 7.34 (t, 2H, *J*=7.8 Hz, ArH), 3.98 (dd, 4H, *J*=15.7, 11.3 Hz, CH), 3.42–3.22 (m, 8H, CH_2), 0.33 and 0.28 (2s, 24H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 155.9, 130.8, 127.2, 127.0, 126.9, 74.3, 37.0, −1.6, −1.6, −1.9, −2.0; FAB-MS (*m/z*) 693.3 (M^++1); IR ($CHCl_3$, cm^{-1}) 2957, 1560, 1438, 1339, 1328, 1303, 1252, 1149, 1104, 903, 896, 883, 873, 841, 814, 789; anal. calcd for $C_{32}H_{44}N_4O_6Si_4$: C, 55.46; H, 6.40; N, 8.08. Found: C, 55.60; H, 6.15; N, 7.60. Compound **6**: mp 261–263°C; ^{1}H NMR (300 MHz, $CDCl_3$) 7.59–7.32 (m, 8H, ArH), 4.08–3.97 (m, 4H, CH), 3.39–3.04 (m, 8H, CH_2), 0.40–0.29 (m, 24H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 156.6, 130.4, 126.7, 125.9, 74.4, 36.9, −0.7, −1.0; FAB-MS (*m/z*) 693.3 (M^++1); IR ($CHCl_3$, cm^{-1}) 2923, 2853, 1597, 1329, 1252, 1104, 874, 842, 789; anal. calcd for $C_{32}H_{44}N_4O_6Si_4$: C, 55.46; H, 6.40; N, 8.08. Found: C, 55.18; H, 6.22; N, 7.59. Compound **8**: ^{1}H NMR (300 MHz, $CDCl_3$) 8.00 (d, 2H, *J*=7.9 Hz, ArH), 7.76–7.67 (m, 4H, ArH), 4.12–3.98 (m, 4H, CH), 3.63–3.20 (m, 8H, CH_2), 0.33–0.26 (m, 24H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 158.0, 149.1, 136.7, 122.1, 74.8, 36.5, −0.8, −1.8, −2.1, −2.5; FAB-MS (*m/z*) 695.2 (M^++1); IR ($CHCl_3$, cm^{-1}) 2959, 2919, 2850, 1579, 1467, 1382, 1340, 1257, 1061, 924, 797; anal. calcd for $C_{30}H_{42}N_6O_6Si_4 \cdot C_2H_5OH$: C, 51.86; H, 6.53; N, 11.34. Found: C, 52.49; H, 6.29; N, 11.23. Compound **9**: ^{1}H NMR (300 MHz, $CDCl_3$) 8.20–8.10 and 7.95–7.89 (2m, 6H, ArH), 4.29–4.15 (m, 2H; CH), 3.29–3.03 and 2.87–2.69 (2m, 4H, CH_2), 0.30, 0.28, 0.10 and 0.07 (4s, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 157.4, 157.3, 150.2, 150.2, 147.2, 143.9, 137.6, 137.5, 123.9, 123.8, 123.0, 122.7, 77.1, 76.9, 35.8, 35.7, −1.4, −1.6; FAB-MS (*m/z*) 509.1 (M^++1); IR ($CHCl_3$, cm^{-1}) 2960, 1583, 1483, 1439, 1373, 1258, 1165, 1065, 992, 924; anal. calcd for $C_{22}H_{24}N_6O_5Si_2$: C, 51.95; H, 4.76; N, 16.52. Found: C, 51.60; H, 4.72; N, 16.25.
7. Crystal data for **3**: $C_{32}H_{44}N_4O_6Si_4$, M=693.07, crystal system: triclinic, space group: $P\bar{1}$, *a*=6.8037(8) Å, α=82.616(2)°, *b*=9.3283(11) Å, β=77.729(2)°, *c*=15.4738(18) Å, γ=78.150(2)°, *V*=953.48(19) Å^3, *Z*=1, d_{calc}=1.230 g cm^{-3}, *T*=298(2) K, Siemens SMART diffractometer with CCD detector, Mo-K_α (λ=0.71073Å), μ=2.04 cm^{-1}, of 3728 measured data, 2750 were independent (R_{int}=0.0196), *R*1 [$I > 2\sigma(I)$]=0.0574, *wR*2 (all data)=0.1297 and GOF=1.161. Crystal data for **9**: $C_{22}H_{24}N_6O_5Si_2$, *M*=508.65, crystal system: triclinic, space group: $P\bar{1}$, *a*=8.6725(2) Å, α=75.9570(10)°, *b*=8.6733(2) Å, β=86.1690(10)°, *c*=17.7650(2) Å, γ=71.1580(10)°, *V*=1226.77(4) Å^3, *Z*=1, d_{calc}=0.689 g cm^{-3}, *T*=193(2) K, Siemens SMART diffractometer with CCD detector, Mo-K_α(λ=0.71073Å), μ=0.95 cm^{-1}, of 5079 measured data, 3725 were independent (R_{int}=0.0130), *R*1 [$I > 2\sigma(I)$]=0.0388, *wR*2 (all data) =0.0997 and GOF=1.104.