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Synthesis of novel tricyclononenes containing alkoxysilyl groups

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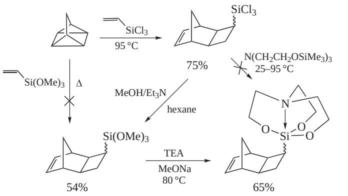
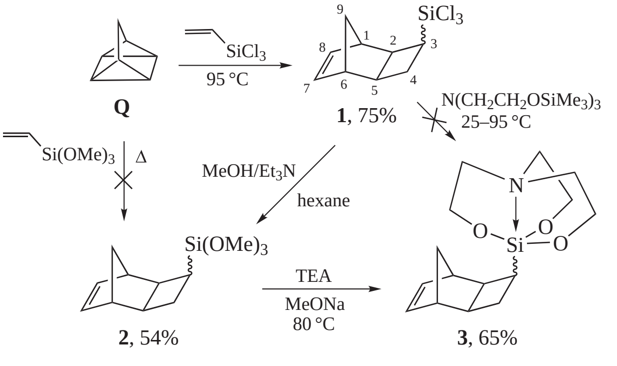
Consequitive treatment of quadricyclane with trichlorovinylsilane and methanol affords 3-trimethoxysilyltricyclo[4.2.1.0^{2,5}]non-7-ene which on reaction with triethanolamine gives a new silatrane promising as a gas separation membrane material.



Functionalized tricyclo[4.2.1.0^{2,5}]non-7-enes are perspective monomers for the development of the wide range of materials.[1] These compounds bearing norbornene fragment turned out to be more active in ring-opening metathesis and addition type polymerizations in comparison with norbornenes. Polymerization according to different routes resulted in the formation of polymers with various backbones possessing different physico-chemical properties.[1(b),2] The discovery of $[2\sigma+2\sigma+2\pi]$-cycloaddition reaction of quadricyclane (**Q**) with activated olefins and alkynes opened a way for selective synthesis of *exo*-tricyclo[4.2.1.0^{2,5}]-nonenes and tricyclo[4.2.1.0^{2,5}]nonadienes.[3] This reaction was extensively used for the preparation of various monomers with different functional groups (*e.g.* silicon-containing, fluorine, carboxy, *etc.*).

Previously we have shown that **Q** did not undergo $[2\sigma+2\sigma+2\pi]$-cycloaddition reaction with vinyltrialkoxysilanes due to weak electron-withdrawing properties of Si(OR)$_3$ group.[4] This observation was contrary to successful Diels–Alder reaction of cyclopenta-1,3-diene with vinyltrialkoxysilanes resulting in the corresponding norbornene derivatives.[5] Therefore, we suggested an indirect method for the synthesis of alkoxysilyl-substituted tricyclononenes (Scheme 1, compounds **2** and **3**).

$[2\sigma+2\sigma+2\pi]$-Cycloaddition reaction of **Q** with trichlorovinylsilane at 95 °C followed by nucleophilic substitution of chlorine atoms in **1**[4] when treated with MeOH in the presence of HCl acceptor (*e.g.* triethylamine) in *n*-hexane afforded a new individual compound, 3-trimethoxysilyltricyclonon-7-ene **2**[†] as a mixture of *syn*/*anti*-isomers (40 : 60) in a moderate yield. This compound could be used as a comonomer or a crosslinking agent for the addition type polymerization of silicon containing norbornenes, which is under investigations.



Scheme 1

Trialkoxysilyl groups are highly reactive and could serve for the further functionalization, in particular for the preparation of silatranes. The silatranes with various substituents are well known compounds which have already been used for different purposes.[6]

Tricyclononene bearing silatranyl group could be in principle synthesized from trichloro (**1**) or trialkoxy (**2**) derivative. However,

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[†] *3-Trimethoxysilyltricyclo[4.2.1.0^{2,5}]non-7-ene* **2**. Absolute methanol (10.8 g, 337.5 mmol) was added dropwise to 3-trichlorosilyltricyclo-[4.2.1.0^{2,5}]non-7-ene **1** (21.0 g, 82.8 mmol) and dry triethylamine (34.3 g, 339.6 mmol) in absolute hexane (200 ml) in the argon atmosphere with strong stirring at room temperature during 40 min. The white precipitate formed was filtered in the argon atmosphere, rinsed by absolute hexane (100 ml). The collected fractions were concentrated under vacuum (1 Torr). The residue was purified by column flash chromatography with hexane as an eluent and distilled under vacuum (1 Torr). The product was obtained as colourless oil. Yield: 10.9 g (54%), bp 80–82 °C (1 Torr). ^{1}H NMR (CDCl$_3$) δ: 5.92–5.85 (m, 2H, C^{7}H, C^{8}H), 3.56 (br. s, 5.4H, OMe), 3.55 (br. s, 3.6H, OMe), 2.77 (s, 0.4H, C^{1}H, C^{6}H), 2.61 (br. s, 0.6H, C^{1}H, C^{6}H), 2.58 (br. s, 1H), 2.19–2.10 (m, 1.4H), 2.06 (d, 0.4H, ^{3}J 9.4 Hz), 2.03–1.97 (m, 2H), 1.86 (d, 0.6H, ^{3}J 9.4 Hz), 1.49–1.44 (m, 1H), 1.26–1.23 (m, 1H), 1.07–1.03 (m, 0.6H). ^{13}C NMR (CDCl$_3$) δ: 135.86, 134.81, 134.79, 134.63 (C^{7}, C^{8}); 50.78, 50.42 (OMe); 45.32, 44.72, 44.49, 44.42 (C^{1}, C^{6}); 40.25, 39.53 (C^{9}); 38.01, 37.39, 36.68, 36.05 (C^{2}, C^{5}); 21.80, 21.09 (C^{4}); 14.62, 14.04 (C^{3}). MS (EI), *m/z* (%): 240 [M]$^{+}$ (5), 121 [Si(OMe)$_3$]$^{+}$ (100), 92 [NBD]$^{+}$ (25), 91 [NBD – H]$^{+}$ (45), 66 [CPD]$^{+}$ (15). Found (%): C, 59.96; H, 8.39. Calc. for C$_{12}$H$_{20}$O$_3$Si (%): C, 59.24; H, 8.27.

3-Silatranyltricyclo[4.2.1.0^{2,5}]non-7-ene **3**. To the mixture of compound **2** (1.02 g, 4.25 mmol) and triethanolamine (0.64 g, 4.25 mmol) in the argon atmosphere, 2 drops of 10% solution of MeONa in MeOH were added at room temperature. The reaction mixture was heated to 80 °C under vacuum (0.07 Torr) and the heating was continued for 30 min. The obtained white crystals were recrystallized from the hexane–chloroform mixture (1 : 2). Yield 0.81 g (65%), mp 201–206 °C. ^{1}H NMR (CDCl$_3$) δ: 5.89–5.81 (m, 2H, C^{7}H, C^{8}H), 3.74 (t, 6H, OCH$_2$, ^{3}J 5.95 Hz), 2.77 (t, 6H, NCH$_2$, ^{3}J 5.95 Hz), 2.59 (br. s, 1H), 2.50 (br. s, 1H), 2.04–1.97 (m, 1H), 1.88–1.85 (m, 3H), 1.38–1.31 (m, 1H), 1.13 (d, 1H, J 8.9 Hz), 0.81–0.73 (m, 1H). ^{13}C NMR (CDCl$_3$) δ: 134.98, 134.42 (C^{7}, C^{8}); 58.06, 51.30 (OCH$_2$, NCH$_2$); 45.55, 44.84; 39.88 (C^{9}); 38.48, 35.58; 22.70 (C^{4}); 20.76. IR (KBr, ν/cm^{-1}): 3052, 2967, 2935, 2883, 2861, 1560, 1484, 1458, 1386, 1351, 1320, 1269, 1249, 1218, 1203, 1122, 1090, 1056, 1024, 992, 947, 914, 891, 794, 780, 757, 710, 674, 647, 629. MS (EI), *m/z* (%): 293 [M]$^{+}$ (0.06), 174 [(SiOCH$_2$CH$_2$)$_3$N]$^{+}$ (100). Found (%): C, 61.58; H, 7.92; N, 4.77. Calc. for C$_{15}$H$_{23}$NO$_3$Si (%): C, 61.40; H, 7.90; N, 4.77.

treatment of **1** with *O*,*O*,*O*-tris(trimethylsilyl)triethanolamine did not lead to silatrane **3**. The corresponding reaction did not proceed at room temperature at all in contrast to methyltrichlorosilane which readily underwent it at room temperature.[7] Heating of **1** and $N(CH_2CH_2OSiMe_3)_3$ resulted in the formation of an insoluble product. The excellent conditions for the selective formation of **3** were found when **2** was applied as an initial compound. Treating it with triethanolamine in the presence of catalytic amounts of MeONa gave new silatranyl-containing tricyclononene **3** in a good yield. It was isolated as an individual compound and characterized with ^1H, ^{13}C NMR, IR spectroscopy as well as X-ray analysis. According to DSC and NMR analysis the product was obtained as a mixture of *syn*/*anti*-isomers in the ratio of about 5 : 95. This indicates that tricyclononene with bulky silatranyl group was preferably formed from the less hindered *anti*-isomer of **2**. The X-ray structure of **3** is presented in Figure 1.[‡] It can be seen that the size of silatranyl group is comparable with that of tricyclononenyl moiety. Silatranyl-containing tricyclononene **3** was soluble in chloroorganic solvents, less soluble in THF or MeOH and insoluble in *n*-hexane, toluene.

Among variable parameters of the silatrane structure the length of Si–N bond is an interesting one depending on the nature of substituent X in $(NCH_2CH_2O)_3SiX$. It is known that the electron properties of substituents as well as steric factors influence the observed coordination between Si and N atoms and, correspondingly, the bond length. Electron-donating substituents increase the length of Si–N bond, while electron-withdrawing groups decrease it (Table 1).

The Si–N bond length in **3** is 2.176 Å. It means that tricyclononenyl moiety impact is close to that of a long alkyl chain (see Table 1), herewith some steric hindrances occur. It resulted in small increase of Si–N bond length.

FT-IR spectrum of silatrane **3** was recorded in the range of 4000–450 cm^{-1}. The presence of symmetric deformational vibration peak of the silatranyl skeleton possessing transannular $N \rightarrow Si$ bond was observed at 575 cm^{-1} (usually it is in the 610–570 cm^{-1} region for silatranes[9]). The Si–O stretching vibrations are assigned to the bands present in 1100–1075 cm^{-1} region, while in **3** it is observed at 1090 cm^{-1}. IR spectra exhibit characteristic absorption norbornene bands. The bands at 1560 cm^{-1} and 3056 cm^{-1} allowed one to unambiguously define the tricyclononene double bonds.

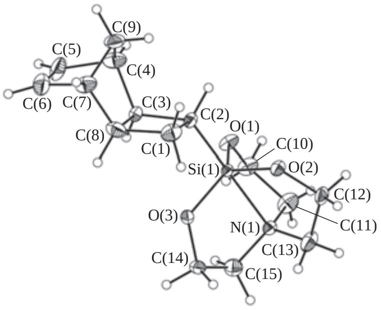
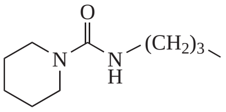
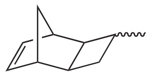


Figure 1 General view of **3** in representation of atoms *via* thermal ellipsoids at 50% probability level.

Table 1 Si–N bond lengths in $(NCH_2CH_2O)_3SiX$.

Substituent X	Si–N bond length/Å	Reference
H	2.301	8
Me	2.412	8
Cl	2.370	8
	2.173	9
	2.176	This work

Tricyclononene bearing Si–OAlk or atrane groups are interesting monomers in the synthesis of polymers for membrane gas separation because side Si–O bonds provide solubility of controlled gas permeation of light hydrocarbons.[10] The preparation and properties of polymers based on the synthesized tricyclononenes would be considered in future works.

In conclusion, the selective method for synthesis of alkoxysilyl functionalized tricyclononenes was developed and tricyclononenes bearing OAlk or atrane groups were obtained. These compounds seem to be promising monomers for the synthesis of polymers for membrane gas separation or can serve as cross-linking agents.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.11.024.

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[‡] *Crystal data for* **3**. Monocrystal of **3** for X-ray analysis was obtained after slow evaporation of MeOH from the solution, $M = 293.43$, monoclinic, space group $P2_1/c$. At 120(2) K: $a = 6.8473(5)$, $b = 16.3825(12)$ and $c = 13.2215(10)$ Å, $\beta = 102.171(2)°$, $V = 1449.80(19)$ Å^3, $Z = 4$, $d_{calc} = 1.344$ g cm^{-3}, $\mu = 0.169$ mm^{-1}. 14848 reflections were collected at $2.007 < \theta < 26.995°$. 3161 independent reflections ($R_{int} = 0.0732$). The structure was refined with full-matrix least-squares on F^2, GOF = 1.059, $R_1 = 0.1005$ and $wR_2 = 0.1936$ (all data), $R_1 = 0.0767$ and $wR_2 = 0.1787$ $[I > 2\sigma(I)]$. For more details, see Online Supplementary Materials.

CCDC 1472193 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.