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$[2\sigma + 2\sigma + 2\pi]$ -Cycloaddition of quadricyclane to partially methylated chlorosilylalkenes

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 $[2\sigma + 2\sigma + 2\pi]$ -Cycloaddition of quadricyclane to trissilylated ethenes $Cl_{3-n}Me_nSiCH=CSiMe_nCl_{3-n}(SiMe_{3-n}Cl_n)$ (n = 1, 2) at 95 °C affords 3,3,4-trissilylated *exo*-tricyclo[4.2.1.0^{2,5}]non-7-enes. Tetrakis(trichlorosilyl)ethene does not react with quadricyclane.

Discovery of $[2\sigma+2\sigma+2\pi]$ -cycloaddition reaction of quadricyclane (**Q**) with olefins opened a way for selective synthesis of *exo*-norbornene derivatives (so-called tricyclononenes).¹ These compounds turned out to be active monomers in addition and ring-opening metathesis polymerizations.² Apparently, their activity can be attributed to the *exo*-configuration of the fused cyclobutane ring and remoteness of the bulky/electron-withdrawing substituents from the double bond. This results in lowering their sterical hindrance effect in a polymerization process. Providing the stereo/regioselectivity and distancing double bond of norbornene fragment from substituents in 3,4 positions,^{1,3} the $[2\sigma+2\sigma+2\pi]$ -cycloaddition of **Q** became the extensively used tool in designing new polymer materials such as photoresists,⁴ optical materials,⁴ membranes,⁵ *etc*.

Earlier, we have shown that polymers bearing SiMe₃ groups synthesized from *exo*-tricyclononene type monomers possessed high gas permeability.^{2(b),5(b)} Furthermore, the gas permeability values were getting higher with increasing a number of siliconcontaining substituents (*e.g.*, SiMe₃, SiPr¹₃) in a monomer unit from one to two.^{2(b)} These observations allowed for assumption that synthesis of the corresponding polymers having three or four SiMe₃ groups per a monomer unit could improve their membrane properties. The findings described below discuss a possibility of synthesis of such *exo*-tricyclononene monomers with three and four silyl groups based on the condensation of **Q** and silylated alkenes **1–3**⁶ (Schemes 1, 2).[†]

Recently, we have demonstrated that some alkenes bearing three silicon groups could react with \mathbf{Q} .⁷ However, further methylation of the corresponding products met difficulties due to high sterical hindrance of starting chlorine-containing silicon groups. Therefore, the initial use of partially methylated chlorosilylalkenes in the reaction with \mathbf{Q} seemed attractive in view of the following exhaustive methylation of the cycloadducts.

In fact, tris-silylated alkenes 1 and 2 readily react with Q at 95 °C (Scheme 1). The reactivity of 1 containing in total four Me groups at Si atoms was noticeably higher than that of alkene 2 with five Me groups. Thus, 50% conversion of 1 was achieved within 15 h, whereas in case of 2 the same conversion was reached only within 90 h. At the same time, both alkenes



1 and **2** were less active than 1,1,2-tris(trichlorosilyl)ethylene because of weaker electron-withdrawing ability of SiMeCl₂ and SiMe₂Cl groups. Therefore, they reacted with **Q** only at elevated temperature (95 °C).

New cycloadducts **4** and **5** were successfully obtained as thermally stable compounds in 55–85% yields, both being formed as individual *anti*-isomers with no admixture of *syn*-isomers. Their configuration was confirmed by ¹H and ¹³C NMR spectroscopy. The possible reason for this is a steric hindrance between



Scheme 2

 $^{^\}dagger$ The cycloaddition reactions were performed according to the earlier developed procedures.^7

 C^9H_2 moiety and a silyl group at C^4 driving the process to *syn*isomer. The further methylation of the obtained cycloadducts 4^{\ddagger} and $5^{\$}$ afforded the desired monomer⁷ **6** bearing three SiMe₃ groups.

The reaction of **Q** with tetrakis(trichlorosilyl)ethene **3** was anticipated to give a tetrasubstituted cycloadduct. Compound 3^{T} was cleanly synthesized according to Scheme 2.⁸ Note that direct synthesis⁹ of this compound is accompanied by formation of hardly separable by-products which could also react with **Q**.

Taking into consideration the fact that reactivity of alkenes gradually increased from vinyltrichlorosilane to 1,1-bis(trichlorosilyl)ethene and then to 1,1,2-tris(trichlorosilyl)ethene,^{7,10} we suggested that olefin **3** would be sufficiently active in the reaction with **Q**. Unexpectedly, no reaction between **3** and **Q** was observed at both room and elevated temperatures (Scheme 3).



The origin of such inactivity can in principle arise from a steric hindrance of substituents and low polarization of the double bond. The possibility of such reaction was evaluated applying density functional theory (DFT)^{††} (Table 1). According to calculations, the lowest activation barrier was attributed to tris-(trichlorosilyl)ethene which showed the highest activity in the studied reaction.⁷ The rise in number of SiCl₃ groups up to four dramatically influenced the activation barrier: it suddenly

[‡] 3-Dimethylchlorosilyl-3,4-bis(methyldichlorosilyl)tricyclo[4.2.1.0^{2,5}]non-7-ene 4: yield 85%, mp 152-155°C. ¹H NMR (499.8 MHz, C₆D₆) δ: 5.80-5.71 (m, 2H, C⁷H, C⁸H), 3.19 (br.s, 1H, C¹H/C⁶H), 2.72 (br.s, 1H, C¹H/C⁶H), 2.56 (d, 1H, C²H, ³J 10.1 Hz), 2.47–2.41 (m, 1H, C⁵H), 2.28–2.21 (m, 2H, C⁹H, C⁴H), 1.31 (d, 1H, C⁹H, ²J 9.6 Hz), 0.84 (br.s, 3 H, MeSiCl₂), 0.77 (br.s, 3 H, MeSiCl₂), 0.55 (br.s, 3 H, Me₂SiCl), 0.52 (br.s, 3 H, Me₂SiCl). ¹³C NMR (125.7 MHz, C₆D₆) δ: 136.53, 134.95 (C⁷, C⁸), 45.43 (C¹, C⁶), 43.73 (C⁴), 42.26 (C⁹), 39.23 (C⁵), 35.20 (C²), 28.37 (C³), 7.79 (MeSiCl₂), 6.58 (MeSiCl₂), 6.29 (Me₂SiCl), 5.84 (Me₂SiCl). § 3,4-Bis(dimethylchlorosilyl)-3-methyldichlorosilyltricyclo[4.2.1.0^{2,5}]non-7-ene 5: yield 55%. ¹H NMR (499.8 MHz, C₆D₆) δ: 5.80-5.71 (m, 2 H, C^7 H, C^8 H), 3.20 (br.s, 1H, C^1 H/ C^6 H), 2.72 (br.s, 1H, C^1 H/ C^6 H), 2.35 (d, 1H, C⁹H₂, ²J 10.1 Hz), 2.32–2.29 (m, 2H), 2.11 (d, 1H, ³J 5.2 Hz), 1.35 (d, 1H, C⁹H, ²J 10.1 Hz), 0.77 (m, 3H, MeSiCl₂), 0.58 (br.s, 3H, Me2SiCl), 0.54 (br.s, 3H, Me2SiCl), 0.46 (br.s, 3H, Me2SiCl), 0.42 (br.s, 3 H, Me₂SiCl). ¹³C NMR (125.7 MHz, C₆D₆) δ: 136.55, 134.92 (C⁷, C⁸), 45.65, 45.37, 43.03, 42.35 (C⁹), 39.24, 33.35, 27.84 (C³), 10.11 (MeSiCl₂), 4.34 (Me₂SiCl), 3.98 (Me₂SiCl), 2.85 (Me₂SiCl), 2.76 (Me₂SiCl).

[¶] Bis(trichlorosilyl)methane. ¹H NMR (499.8 MHz, CDCl₃) δ : 1.37 (s, 2 H). ¹³C NMR (125.7 MHz, CDCl₃) δ : 22.07. ²⁹Si NMR (99.3 MHz, CDCl₃) δ : 1.9.

Dichlorobis(trichlorosilyl)methane. ¹³C NMR (125.7 MHz, CDCl₃) δ : 63.98. ²⁹Si NMR (99.3 MHz, CDCl₃) δ : –9.2.

Tetrakis(*trichlorosilyl*)*ethene* **3**. Copper powder (50 μm) (3.5 g, 55 mmol) and dichlorobis(trichlorosilyl)methane (7.5 g, 21 mmol) were placed in a two-necked flask equipped with magnetic stirrer and reflux condenser. The mixture was heated at 220 °C for 6 h. The crude mixture was extracted with warm hexane (3×15 ml). The solvent was removed under reduced pressure (2 Torr) and the crude product was sublimed (0.1 Torr, 70 °C). Then it was recrystallized twice from hexane and obtained as a moisture sensitive white solid; mp 150–153 °C. Yield: 3.6 g (60%). ¹³C NMR (125.7 MHz, CDCl₃) δ: 178.10. ²⁹Si NMR (99.3 MHz, CDCl₃) δ: –12.2. ^{††} The Cluster of the Novosibirsk University Scientific Computing Center (http://www.nusc.ru/) was used for calculation. Visualization and *xyz*-coordinates of all structures are available from http://limor1.nioch.nsc.ru/ quant/222/. DFT calculations were performed with the PRIRODA program,¹¹ functional PBE,¹² basis L1¹³ (Λ01, cc-pVDZ analog).

Table 1 DFT calculations of activation energies for the reactions of different alkenes with \mathbf{Q} .

Alkene	Activation energy/ kcal mol ⁻¹	Alkene	Activation energy/ kcal mol ⁻¹
H ₂ C=CH ₂	29.8	Cl ₃ Si Cl ₃ Si SiCl ₃	15.8
SiCl ₃	22.3	Cl ₃ Si Cl ₃ Si SiCl ₃	33.4
SiCl ₃	16.8	Cl ₃ Si Cl ₃ Si SiMe ₃	34.3

increased by more than twice (from 15.8 up to 33.4 kcal mol⁻¹). This barrier is even higher than that for unsubstituted ethylene (29.8 kcal mol⁻¹). A possible reason of this fact lies in a high steric hindrance of four SiCl₃ substituents. Indeed, according to X-ray data, C and Si atoms of alkene **3** are not in the same plane. The double bond showed the twist with dihedral angles Si¹–C=C–Si³ of 28.0° and Si²–C=C–Si⁴ of 28.2°.⁸ Non-planar structure of **1** resulted in the creation of a critical hindrance for the desired reaction. Replacement of one SiCl₃ group by SiMe₃ group makes double bond more polar. However, in this case a growth of activation barrier was observed (see Table 1). This can be attributed to electron-donating properties of SiMe₃ group, and this fact evidenced that steric hindrance is the principal factor.

In summary, it was shown that partially methylated chlorosilylalkanes bearing three Si-containing substituents at the double bond and up to five Me groups at Si atoms can successfully give $[2\sigma+2\sigma+2\pi]$ -cycloadducts with **Q**, while the alkene with four strong electron-withdrawing SiCl₃ groups turned out to be inactive at all due to greater steric hindrance.

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