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Tris(t-butyldimethylsilyl)trimethylsilylethylene and Tetrakis(dimethylsilyl)ethylene. The Most Twisted and Untwisted Tetrasilylethylenes[1)]

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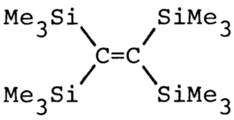
Tris(t-butyldimethylsilyl)trimethylsilylethylene and tetrakis(dimethylsilyl)ethylene were prepared. Structures of these most twisted and untwisted olefins are determined by X-ray diffraction.

Previously we have reported syntheses and properties of tetrakis(trimethylsilyl)ethylene (**1**),[2)] 1,1-bis(t-butyldimethylsilyl)-2,2-bis(trimethylsilyl)ethylene (**2**),[3)] Z-1,2-bis(t-butyldimethylsilyl)-1,2-bis(trimethylsilyl)ethylene (**3**)[4)] and other tetrasilylethylenes as a new class of overcrowded olefins. The structures of these olefins are of interest to investigate how the molecules relieve their inherent repulsive nonbonded interactions. We have observed that nonplanar distortion (twisting) is the main factor for relieving the overcrowdness for **1** (29.5°) and **2** (49.6°) but slight pyramidalization starts to occur for **3** in addition to twisting.

We now report herein preparation and properties of tris(t-butyldimethylsilyl)trimethylsilylethylene (**4**) and tetrakis(dimethylsilyl)ethylene (**5**). The former is the most twisted and congested olefins so far prepared and the latter is the reference untwisted tetrasilylethylene.



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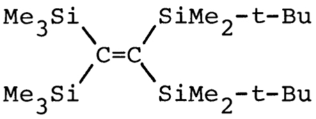

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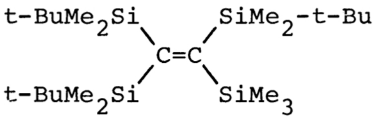

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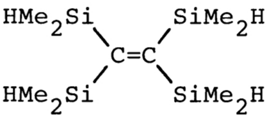
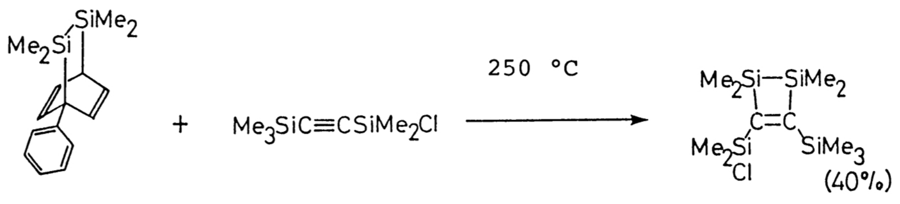


5

First 1-(chlorodimethylsilyl)-2-(trimethylsilyl)-3,3,4,4-tetramethyl-3,4-disilacyclobutene (**6**) was prepared by the reaction of 1-phenyl-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octadiene (**7**) and (chlorodimethylsilyl)trimethylsilylacetylene (**8**) (Eq. 1). A dichlorodisilacyclobutene (**9**) was prepared similarly (Eq. 2).



(1)

7 **8** **6**

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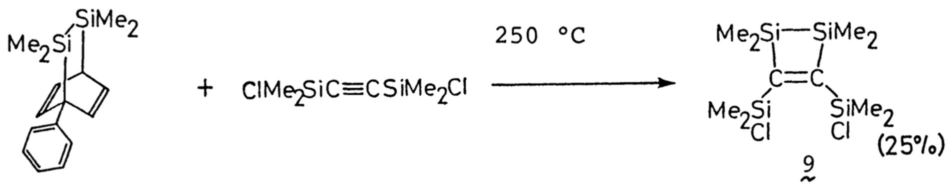
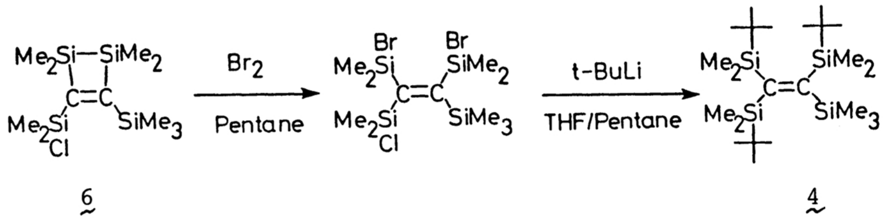


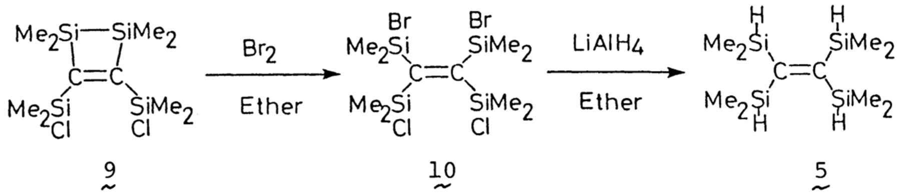
(2)

The compound **6** was isolated as a mixture with a small amount of biphenyl. The reaction of **6** with bromine (0.95 equiv.) at 0 °C resulted in the formation of a yellow homogeneous solution, to which excess t-butyllithium in pentane and a small amount of THF were added at room temperature under argon (Eq. 3). Low boiling materials were removed by distillation (Kugel rohr) and the residue was treated by column chromatography on silica gel with hexane followed by HPLC (inverse phase with methanol) to give red-brown solid. Recrystallization from ethanol gave a pure sample (**4**) in 2% yield.5)



(3)

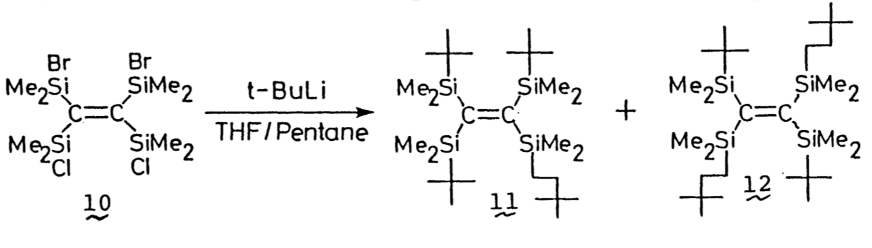
The reaction of **9** with bromine (0.95 equiv.) gave 1,2-bis(bromodimethylsilyl)-1,2-bis(chlorodimethylsilyl)ethylene (**10**), the formation of which was evidenced by reduction with lithium aluminum hydride to give tetrakis(dimethylsilyl)ethylene (**5**) as colorless crystals in 80% yield (Eq. 4).6)



(4)

The reaction of **10** with t-butyllithium did not afford the expected tetrakis(t-butyldimethylsilyl)ethylene and instead new tetrasilylethylenes, **11** and **12**, were obtained in very low yields (Eq. 5). Introduction of the 3,3-dimethylbutyl group may be rationalized by the formation of the corresponding organolithium compounds by the reaction of t-butyllithium with ethylene formed by the decomposition of THF.

Compounds **4** and **5** are thought to be the most twisted and untwisted tetrasilylethylenes and therefore their structures are of interest in comparison with other previously prepared olefins. Figures 1 and 2 show ORTEP drawings of **4** and **5** determined by X-ray diffraction analysis,7) together with pertinent bond data.



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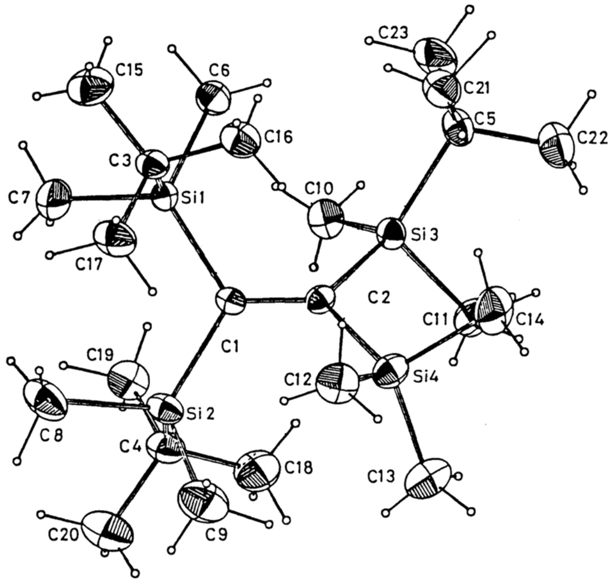
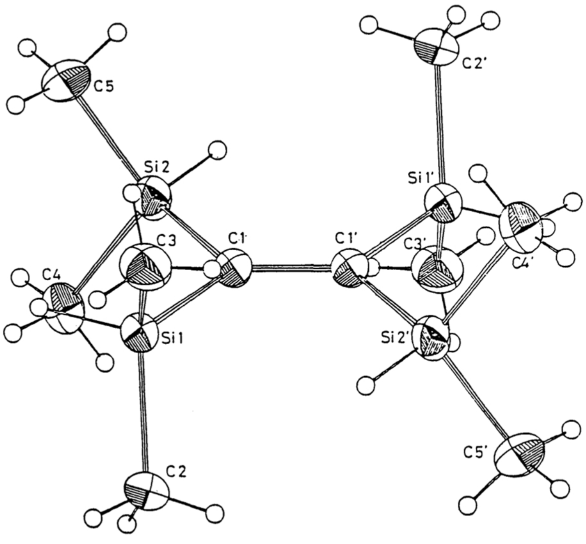


Si1-C1	1.913(6)	C2-Si3-C5	124.8(3)
Si2-C1	1.946(7)	C10-Si3-C5	99.5(3)
Si3-C2	1.963(7)		
Si4-C2	1.971(7)		
Si3-C5	1.960(8)		
C1-C2	1.381(9)		

Fig. 1. ORTEP diagram of 4 and selected bond lengths (Å) and bond angles (°) with esd's in parentheses.



Si1-C1	1.884(7)
Si2-C1	1.917(7)
C1-C1'	1.367(9)
Si1-C1-C1'	126.3(3)
Si2-C1-C1'	119.8(3)

Fig. 2. ORTEP diagram of 5 and selected bond lengths (Å) and bond angles (°) with esd's in parentheses.

No twisting around the double bond was observed for 5, as expected, while 4 shows several unusual structural features in addition to large twisting. The C1 carbon of 4 is almost planar with similar steric arrangement of the corresponding carbon atoms of 2.$^{3)}$ Thus two t-butyl groups have perfect anti-conformation, while steric hindrance of the molecule seemed to be concentrated intensively around the C2 atom of the double bond. The C2 carbon shows pyramidalization rather in a large extent. Bond lengths of C2-Si3 and Si3-C5 are very much elongated to 1.963 and 1.960 Å, respectively. These values are comparable to the longest Si-C bond length reported recently for hexa(t-butyl)cyclotrisilane (1.970 Å)$^{8)}$ and hexa(t-butyl)disilane (1.99 Å).$^{9)}$ The bond angles of C2-Si3-C5 (124.8°) and C10-Si3-C11 (99.5°) are also unusual.

As we have reported previously,$^{3)}$ rearrangement took place in the formation of 2 from 1,2-bis(bromodimethylsilyl)-1,2-bis(trimethylsilyl)ethylene. Intensive steric distortion around the C2 of 4 might suggest that in the formation of 4 similar rearrangement occurred for bromodimethylsilyl groups in the step of introducing two t-butyl groups. The last t-butyl group was then introduced. The last t-butyl group seems to be resigned to severe steric hindrance as if it sneaked in.

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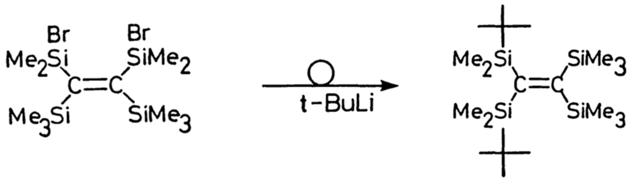

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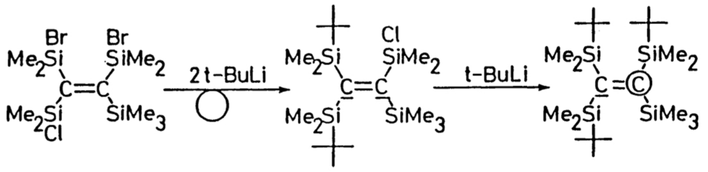

(7)

$\underline{C}$: planar carbon

Ⓒ : pyramidalized carbon

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5) **4**: red crystals; mp 83-85 °C; ^{1}H NMR ($CDCl_3$) δ 0.26 (6H, s), 0.34 (21H, s), 0.87 (9H, s), 0.92 (9H, s), 1.06 (9H, s); ^{13}C NMR ($CDCl_3$) δ 0.91, 1.83, 3.59, 6.59, 20.8, 21.0, 28.7, 29.1, 30.3, 209.8, 213.4; ^{29}Si NMR ($CDCl_3$) δ -10.91, -5.53, -1.90, -1.40; UV (hexane) λ_{max} (ε) 250 sh (7300), 434 (400) nm; MS m/z (%) (12 eV) 385 (M^+-t-Bu, 3.2), 327 (100).

6) **5**: colorless crystals; mp 73-74 °C; ^{1}H NMR ($CDCl_3$) δ 0.25 (24H, d, J = 3.9 Hz), 4.37 (4H, sep, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ -2.15, 184.8; ^{29}Si NMR ($CDCl_3$) δ -24.5; UV (hexane) λ_{max} (ε) 225 (16200), 341 (220) nm; MS m/z (%) 260 (M^+, 3.8).

7) For X-ray analysis, intensities were measured on a Rigaku diffractometer using MoK_α radiation at 13 °C for **4** and at -60 °C for **5**. Independent reflections within $|\underline{Fo}| \geqq 3\sigma\ |\underline{Fo}|$ were used in the structure refinement.
Crystal data of **4**: $C_{23}H_{54}Si_4$, Fw 442.98, space group P_{bca}, a = 17.817 (2) Å, b = 30.140 (2) Å, c = 10.901 (1) Å, V = 5800.2 (6) Å^3, Z = 8, d_{calcd} = 1.01 g cm^{-3}, crystal dimension 0.25x0.25x0.30 mm^3. Numbers of observed data = 3657 ($2\theta \geqq 55°$). The final R factor was 0.087.
Crystal data of **5**: $C_{10}H_{28}Si_4$, Fw 260.65, space group $P2_1/n$, a = 8.496 (1) Å, b = 16.255 (1) Å, c = 6.554 (1) Å, β = 107.75° (1), V = 862.1 (3) Å^3, Z = 2, d_{calcd} = 1.00 g cm^{-3}, crystal dimension 0.2x0.2x0.2 mm^3. Numbers of observed data = 1881 ($2\theta \geqq 55°$). The final R factor was 0.093.

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