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GENERATION AND REARRANGEMENT OF A 1-NORBORNENE IN PYROLYSIS OF 1-SILA-2-OXYNORBORNANES

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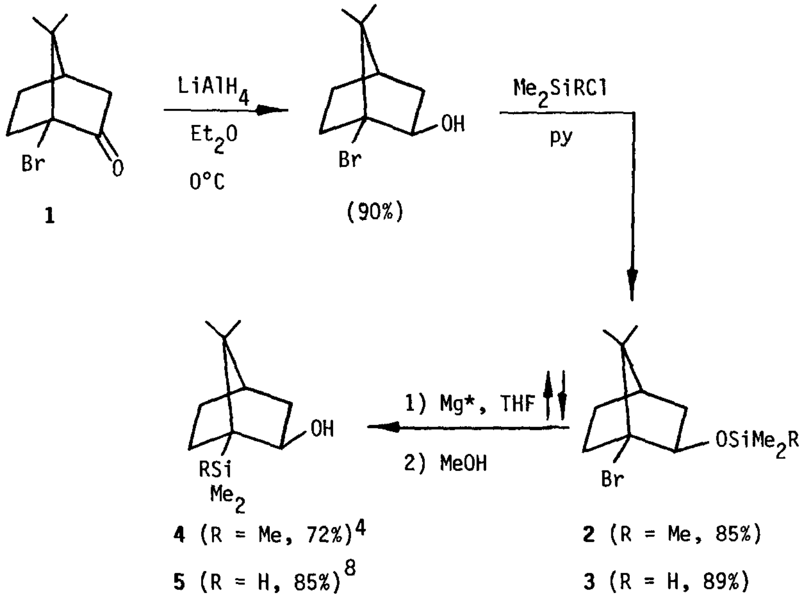
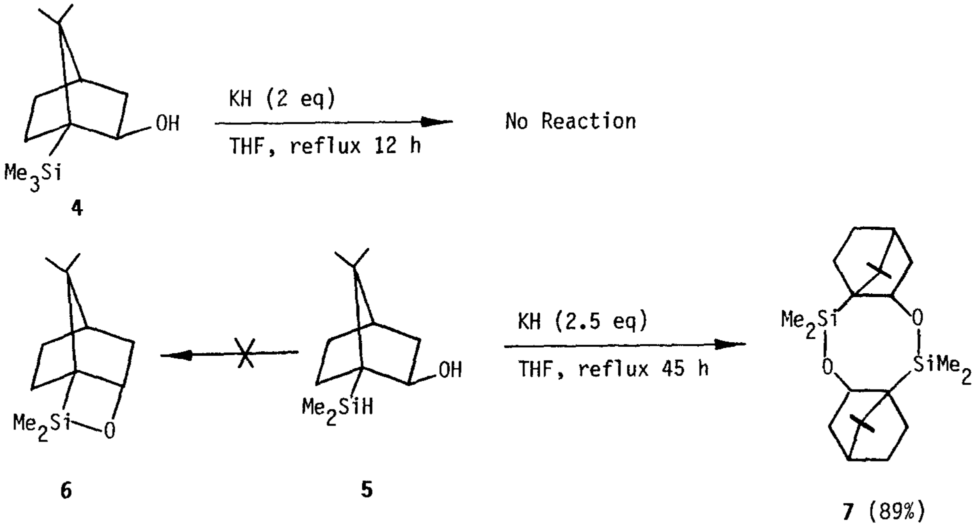
Abstract: Gas phase pyrolysis of 1-sila-2-oxynorbornenes yields a nortricyclene which is proposed to arise from a β-elimination to form a 1-norbornene, which isomerizes to a 2-norbornacylidene which undergoes γ-CH insertion.

Extension of Peterson Olefination to the conversion of β-hydroxysilanes into alkenes has proven to be an extremely useful procedure in organic synthesis.[1] We have begun to explore the possibility of using this procedure in the synthesis of anti-Bredt olefins. Toward this end, 1-trimethylsilyl-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (**4**) was synthesized, starting with bromoketone **1**,[2] by the procedure outlined in Scheme 1.[3]

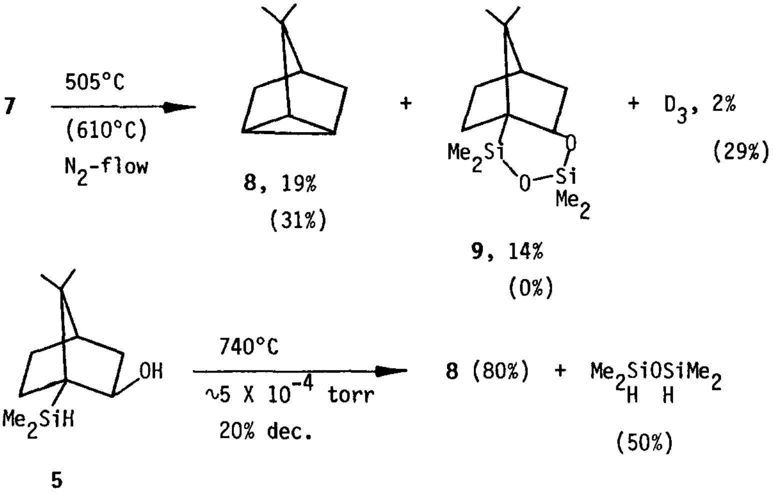
Scheme 1



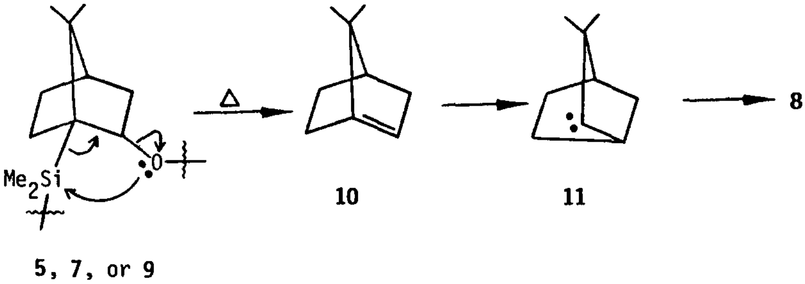
Since KH is well known to be an efficient reagent for the conversion of β-hydroxysilanes to olefins,[7] a THF mixture of 4 and a two-fold excess of KH was refluxed overnight. Analysis by GCMS revealed that virtually all of 4 remained intact, and thus a perhaps unsurprising limitation to this route to olefins was realized. In contrast, the reaction of KH and the dimethylsilyl analog 5[8] appeared to begin upon mixing. It was hoped that 5 would undergo a base-induced intramolecular etherification to produce silaoxetane **6**. Instead, etherification occurred in a bimolecular fashion to afford the cyclic silyl ether 7 as an inseparable mixture of syn- and anti-isomers (4:5 by PMR) in 89% yield after refluxing for 45 hours.



Based on our earlier experience with cyclic ethers of this type,[9] we thought it possible that pyrolysis of 7 would result in olefin extrusion. Pyrolysis of 7 (30 mg) was conducted by slow, dropwise addition into a vertical, quartz chip packed tube at 505°C continuously swept with a 32 mL/min flow of nitrogen. Mass recovery was low due to the small sample size, but the GC trace of the pyrolysate was very clean, showing only two major products, nortricyclene 8 (19%) and cyclic disiloxane 9 (14%). Identification of 9 was accomplished by independent synthesis, while 8[10] was spectrally compared with an authentic sample. Pyrolysis of 7 at 610°C raised the yield of 8 to 31%, completely eliminated 9 from the product mixture, and afforded hexamethylcyclosiloxane, D_3, in 29% yield along with a few percent of D_4. Similar behavior was found in the flash vacuum pyrolysis (FVP) of 5 which at 740°C (ca. 5×10^{-4} torr) decomposed to the extent of 20% to afford 8 (16%, 80% corrected) and sym-tetramethyldisiloxane (10%, 50% corrected). Likewise, FVP (760°C) of 4 produced 8 (17%) and hexamethyldisiloxane (28%), but this pyrolysis was much less clean than that of 5.



As to the intriguing origin of nortricyclene **8**, we can think of no alternative to intramolecular C-H insertion by 2-norbornanylidene **11**. It is well established that such carbenes efficiently undergo γ-CH insertion to afford nortricyclenes.[11] The origin of **11** is less obvious, but we suggest that it arises from rearrangement of 1-norbornene **10** via a 1,2-alkyl shift. Although thermal isomerization of an olefin to a carbene is hardly a common reaction, we note a close precedent reported by Chan,[12] who has presented strong evidence that a bicyclo[2.2.2]oct-1-ene isomerized to a bicyclo[3.2.1]octanylidene by an analogous process. Thus, it is our current thinking that **5**, **7**, and **9** undergo thermally-induced elimination to produce **10**[14] which owing to its considerable strain is prone to rearrangement to carbene **11** which cyclizes to the observed product. We are currently attempting to extend this route to other strained olefins.



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3. The key step of this sequence is the conversion of the β-bromoether **2** to the desired β-silyl alcohol **4**.[4] Following the work of Speier,[5] this was accomplished in 72% yield by the action of activated magnesium[6] in refluxing THF.
4. **4**: mp 35-9°C; ^{1}H NMR ($CDCl_3$) δ 3.83-3.86 (m, 1H), 1.19 (s, 3H), 0.81 (s, 3H), 1.8-0.9 (m, 7H), 0.06 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 82.05, 48.79, 43.87, 42.77, 29.79, 27.39, 23.29, 22.90, -0.49; calcd for $C_{12}H_{24}SiO$ m/e 212.15965, found m/e 212.15988.
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8. **5**: ^{1}H NMR ($CDCl_3$) δ 3.93 (sept, 1H, J = 3.9 Hz), 3.84 (m, 1H), 1.8-0.9 (m, 7H), 1.19 (s, 3H), 0.90 (s, 3H), 0.15 (d, 3H, J = 3.9 Hz), 0.11 (d, 3H, J = 3.9 Hz); ^{13}C NMR ($CDCl_3$) δ 81.43, 48.47, 47.90, 43.09, 42.51, 29.73, 27.34, 22.58, 22.39, -4.14, -4.68; IR (neat) 3492 cm^{-1} (O-H), 2102 cm^{-1} (Si-H); calcd for $C_{11}H_{21}SiO$ (M^+ - 1) m/e 197.13616, found m/e 197.13575. Anal. Calcd for $C_{11}H_{22}SiO$: C, 66.60; H, 11.18. Found: C, 66.49; H, 11.53.
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