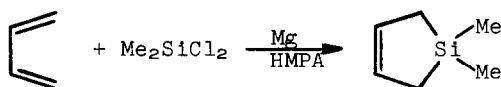


SYNTHESIS AND CHEMISTRY OF 9,9-DIMETHYL-9-SILABICYCLO[4.2.1]NONA-2,4,7-TRIENE

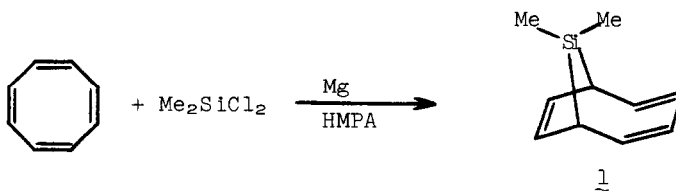
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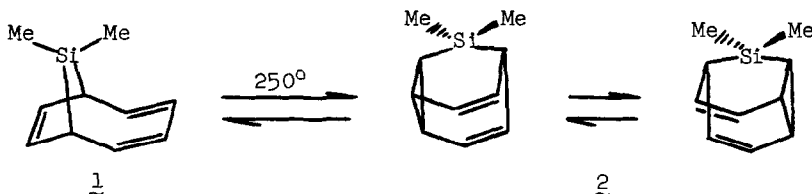
The synthesis of 1,1-dimethyl-1-silacyclopent-3-enes from the alkali metal induced 1,4-addition of dimethyldichlorosilane to 1,3-dienes<sup>1</sup> has been dramatically extended by Dunogues, Calas and coworkers<sup>2</sup> through the use of magnesium as the metal and hexamethylphosphoramide (HMPA) as the solvent. This general reaction opens the way for the synthesis of a wide variety of cyclic, unsaturated organosilanes.



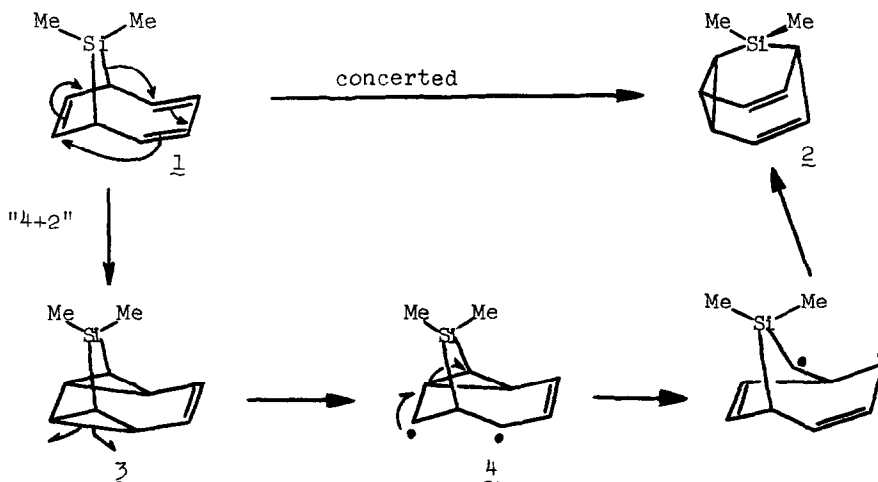
We report here the convenient synthesis of the first example of the 9-silabicyclo[4.2.1]nona-2,4,7-triene (1) ring system through the reaction of dimethyldichlorosilane, magnesium and cyclooctatetraene (COT) in HMPA. In contrast to the usual conditions for dihalosilane addition to conjugated dienes (e.g. 1,4-addition of dimethyldichlorosilane to 1,3-butadiene, using  $\text{Mg}/\text{HMPA}$ , requires 96 hours at reflux for a 20% yield),<sup>2</sup> the reaction of COT, magnesium and dimethyldichlorosilane is decidedly exothermic. The entire reaction requires less than one hour and, after removal of HMPA by aqueous washing, the title compound (1) is obtained in high purity from chromatography on basic alumina in ca. 20% yield,  $m/e$  162.0866, calcd. 162.0865; nmr ( $\text{CCl}_4$ )  $\delta$ 5.60 (6H, m, vinyl),  $\delta$ 1.88 (2H, sym. d of m, bridgehead),  $\delta$ 0.25 (3H, s, Si- $\text{CH}_3$ ),  $\delta$ 0.03 (3H, s, Si- $\text{CH}_3$ ); calcd. for  $\text{C}_{10}\text{H}_{14}\text{Si}$ : C, 74.00%; H, 8.69%; Found: C, 73.92%; H, 8.85%.



At 250° (degassed, sealed tube, diphenylether) 1 is partially converted (46% after 72 hours) into the silabarbarlane (2) in a slow equilibrium process: m/e 162.0864, calcd. 162.0865; nmr (CCl<sub>4</sub>) δ5.54 (2H, broad t, J=8Hz), δ3.78 (4H, broad t, J=8Hz), δ1.18 (2H, broad t, J=8Hz), δ-0.01 (6H, s). The nmr spectrum is quite analogous to that described for barbaralane,<sup>3</sup> 9-thiabarbaralane<sup>4</sup> and 9-phosphabarbaralane.<sup>5</sup> Thus 2 is rapidly undergoing degenerate Cope rearrangement at room temperature. However, at -70° both the pmr and cmr spectra show 2 to be completely "frozen".<sup>9</sup>



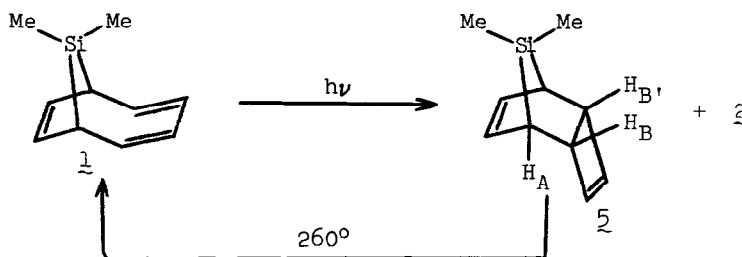
The thermal conversion of 1 to 2 is quite surprising as we know of no previous example of a bicyclo[4.2.1]nonatriene system being thermally transformed into a barbaralane system.<sup>6</sup> One mechanistic possibility for this transformation is a concerted, eight-electron sigmatropic migration of silicon and as such would involve inversion at silicon. However, alternate, stepwise routes are available. For example an intramolecular Diels-Alder reaction to provide 3 which could undergo homolytic cleavage of a cyclopropane bond would afford a diradical of the familiar di-π-methane type, 4, which could undergo simple reorganization to 2.



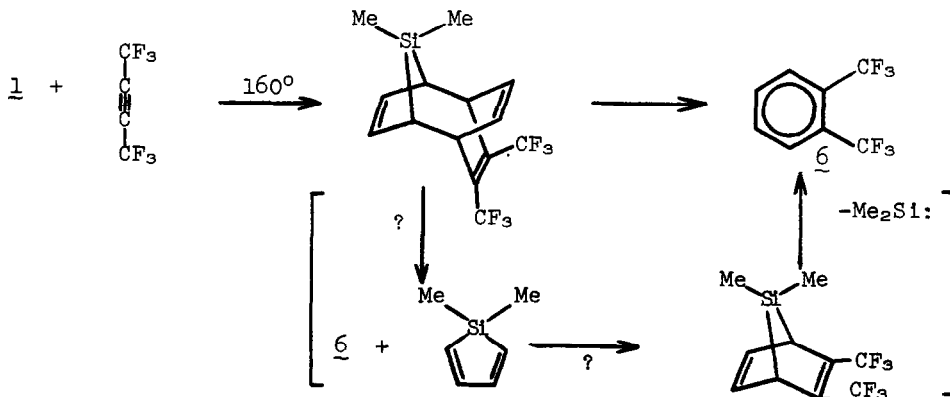
While there are a number of tagging schemes which should allow one to distinguish between the two paths shown here, it should be noted that a 1,2-migration of silicon in diradical 4 would not only provide 2 directly but would yield

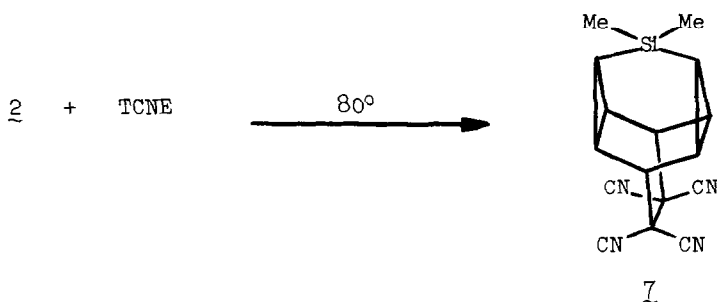
the same tagging results as the concerted route. Therefore, only the stepwise route illustrated here would yield tagging results consistent with maintenance of the integrity of all silicon-carbon bonds. We are presently building the appropriate model systems.

The photochemical conversion of various bicyclo[4.2.1]nonatrienes to the barbarlane ring system has been reported.<sup>7</sup> Irradiation of 1 (450 watt Hanovia lamp) in a variety of solvents, with or without sensitizers, always resulted in complete destruction of 1 and the formation of a mixture of 2 (20%) and the product of intra molecular  $2\pi+2\pi$  cyclization, 5 (80%). The nmr spectrum of 5 makes assignment of endo fusion conclusive as  $J_{AB}$  is 2.7Hz which compares favorably with the same coupling in the carbon analog ( $J_{AB}=3.5\text{Hz}$ , ref. 8) and the phosphorus analog ( $J_{AB}=3.2\text{Hz}$ , ref. 5). Observation of a  $J_{AB'}$  of 1.3Hz is consistent with the W-coupling possible in the endo-isomer.<sup>9</sup> While photostable, 5 is quantitatively converted to 1 after 2.5 hours at 260°.



Not surprisingly, addition of dieneophiles to 1 has proved difficult. Maleic anhydride failed to react after one week at 170°. Hexafluoro-2-butyne reacts incompletely after four days at 160° to yield o-bis(perfluoromethyl)xylylene (6) as the only identifiable (thus far) product. While TCNE fails to react with 1 it smoothly adds to 2 in refluxing benzene to yield the homo-Diels-Alder adduct (7).





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 (d) 9-Phosphabarbarlone: Ref. 5.
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9. Full spectral details will be included in the complete manuscript.