

1-Methyl-1-silatricyclo[3.3.0.0]octa-2,6-diene. A Silasemibullvalene

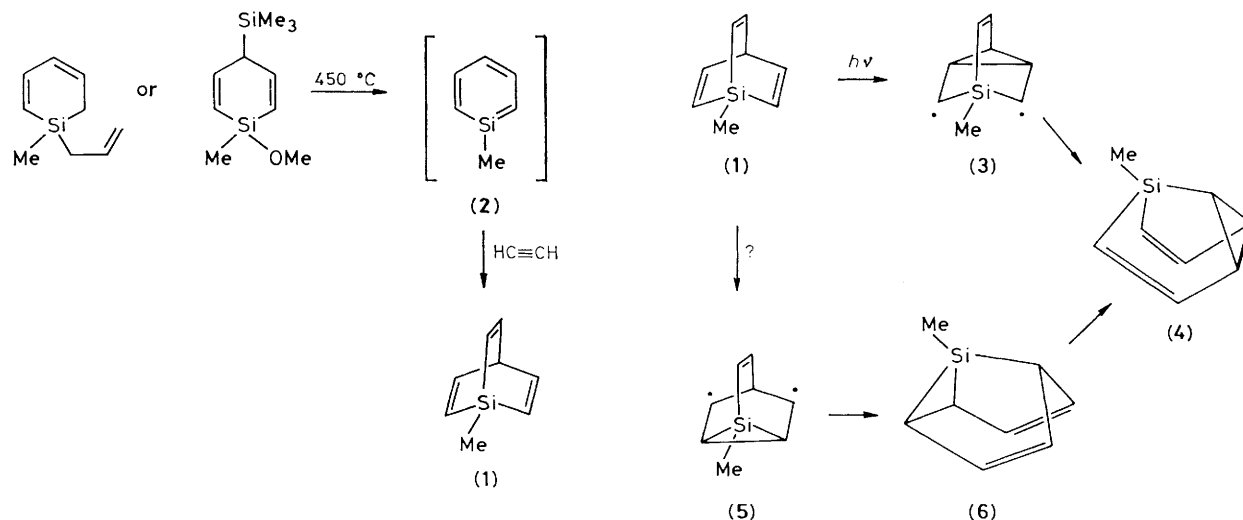
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Sensitized photolysis of 1-methyl-1-silabicyclo[2.2.2]octatriene (silabarrelene) quantitatively affords the first example of a silasemibullvalene; no evidence for thermally induced Cope rearrangement of the title compound was found.

Silabarrelene¹ (**1**) is conveniently prepared through the trapping of thermally generated 1-silatoluene (**2**) in a gas-phase Diels-Alder reaction.^{2,3} We now report that like barrelene,⁴ silabarrelene (**1**) undergoes photochemical rearrangement to

the tricyclo[3.3.0.0]octa-2,6-diene ring system. Thus, irradiation through Pyrex of a degassed solution of (**1**) in cyclohexane with acetone sensitizer (450 W medium-pressure Hg arc) resulted in complete disappearance of (**1**) and quantitative



(by n.m.r. spectroscopy) formation of 1-methyl-1-silatricyclo-[3.3.0.0]octa-2,6-diene (**4**), the first example of a silasemibullvalene. Silasemibullvalene (**4**) was isolated by preparative gas chromatography and identified by its spectral characteristics [^1H n.m.r. (CCl_4) δ 0.4 (s, 3H, SiMe), 1.68 (t, 1H, J 9 Hz), 3.07 (br. d of d, 2H, J 9 Hz and 2 Hz), 5.82 (d, 2H, J 9 Hz), and 6.02 (d of d, 2H, J 9 Hz and 2 Hz); ^{13}C n.m.r. (CDCl_3) δ 141.64, 132.16, 43.37, 28.03, and -5.55 p.p.m.; g.c.m.s. m/z 134 (M^+ , 26%), 119 ($M-\text{Me}$, 100%), 108 ($M-\text{C}_2\text{H}_2$, 57%), 93 ($M-\text{Me}-\text{C}_2\text{H}_2$, 82%), 67 (24%), and 53 (34%)]. The symmetry of barrelene is lost for silabarrelene (**1**), and presumably the initial diradical intermediate in the di- π -methane process is (**3**) rather than (**5**) owing to the considerable ring strain of the silacyclopropane ring.⁵ However, formation of (**6**) followed by rapid Cope rearrangement to (**4**) cannot be excluded.

In striking contrast with semibullvalene, which undergoes a degenerate [3,3] shift at -150 °C with an activation energy of only 4.8 kcal/mol,^{6†} no change in the ^1H n.m.r. spectrum

of (**4**) is observed on heating to $+150$ °C. Thus, it would appear that the strain of a silacyclopropyl ring locks the molecule in structure (**4**), although a very small equilibrium cannot be ruled out at this time.

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References

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† 1 kcal = 4.18 kJ.