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Preliminary communication

2,3-Bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene. A silaalkene generator

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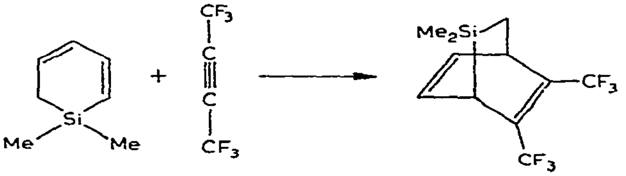
Although molecules containing a silicon–carbon double bond have not been isolated[1], there are several reports of their existence as intermediates in the reactions of dialkyldihalosilanes with alkali metal[2], from α-silyl Grignard reagents[3], and from the pyrolysis of silacyclobutanes[4], tetramethylsilane[5], and allyltrimethylsilanes[6]. The most common evidence cited for the transient existence of silaalkenes is the formation of the head-to-tail dimers, 1,3-disilacyclobutanes. To date the most impressive evidence is found in the kinetic analysis of the thermal decomposition of 1,1-dimethyl-1-silacyclobutane, which cleanly affords 1,1,3,3-tetramethyl-1,3-disilacyclobutane, by Flowers and Gusel'nikov[7]. We report here the synthesis of a new silaalkene generator, and initial observations on its thermal and photochemical decomposition.

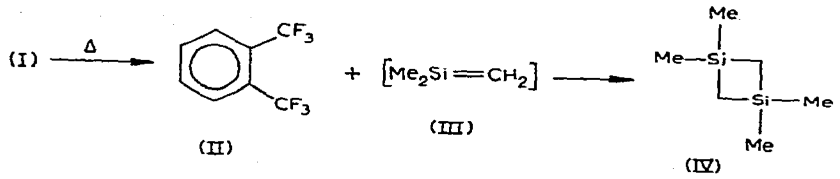
2,3-Bis(trifluoromethyl)-7,7-dimethyl-7-silabicyclo[2.2.2]octa-2,5-diene (I) was prepared from the Diels–Alder addition of 1,1-dimethyl-1-silacyclohexa-2,4-diene[8][★] and excess perfluoro-2-butyne (sealed tube; 4 h at 60°) yield 60.3% of a colorless viscous liquid, m/e M^+ found: 286.0649 (calcd.: 286.0613). (Analysis found: C, 46.14; H, 4.22; Si, 9.78. $C_{11}H_{12}F_6Si$ calcd.: C, 46.14; H, 4.40; Si, 9.67%.)



(I)

[★] This procedure was modified in that dehydrobromination of 1,1-dimethyl-4-bromo-1-silacyclohex-2-ene was accomplished with DBU.

While pyrolysis of (I) under a variety of conditions (both neat and flow) affords *o*-bis(trifluoromethyl)benzene (II) [9]* the cleanest results have been obtained above 400°C in a gas-flow system with a carrier gas (*e.g.* cyclohexane)[10]**. Using these conditions (II) and (IV) are cleanly formed as the sole isolable products in yields of 76% and 94%



respectively (VPC analysis). In the absence of any carrier gas the flow pyrolysis of (I) at 410°C affords isolated yields of (II) (ca. 95%), (IV) (ca. 4%) and a considerable amount (ca. 13%) of high molecular weight material (*m/e* 292, M^+) whose high resolution mass spectrum is consistent with $C_{15}H_{28}Si_3$.

Irradiation of I at 77 K or 28 K (neat, Hg arc through quartz) cleanly affords (II) and (IV) as shown by infrared monitoring. However, initial attempts at solution photochemistry (cyclohexane, 2537 Å) have afforded only traces of (IV) along with large amounts of (II).

Clearly (I) is a very convenient source of 2-methyl-2-silapropene, (III). Experiments designed to determine the effect of varied substitution on ease of thermolysis, yield maximization, and trapping of silaalkenes, are currently in progress.

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*Both II and III were identified by IR, NMR and high-resolution mass spectrometry: (II) *m/e* found: 214.021812, calcd.: 214.021770: (II) *m/e* found: 144.079553, calcd.: 144.078891. Spectra and VPC retention time for (II) were identical with an unambiguously prepared sample[9].

**A very similar decomposition of Si–Si bridged bicyclo[2.2.2]octadiene has been reported to afford a transient silene ($Me_2Si{=}SiMe_2$)[10].

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