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6,6-DIMETHYL-6-SILAFULVENE. GENERATION AND TRAPPING REACTIONS[1]

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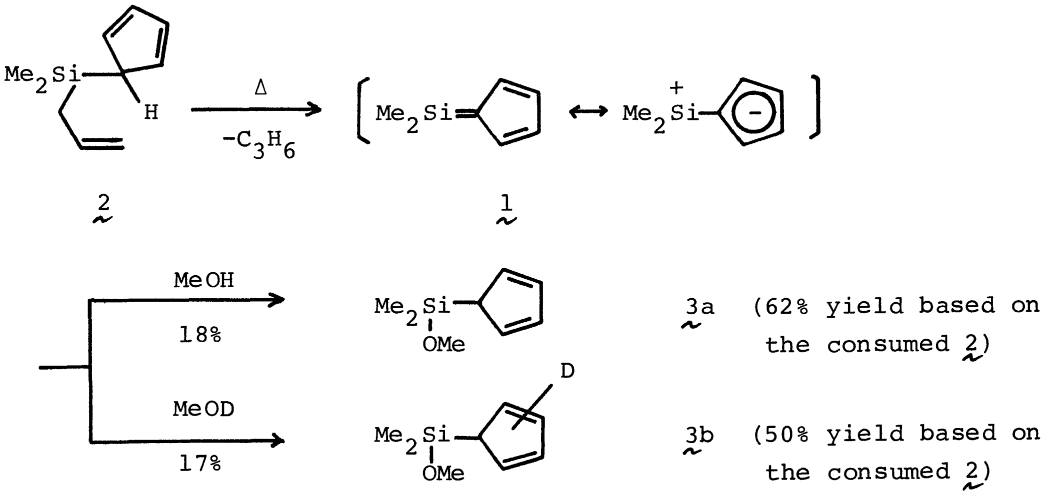
6,6-Dimethyl-6-silafulvene generated from (allyl)(cyclopentadienyl)dimethylsilane reacts with a trapping reagent such as methanol, benzaldehyde, and benzophenone to give (cyclopentadienyl)(methoxy)dimethylsilane, 6-phenylfulvene, and 6,6-diphenylfulvene, respectively. Without a trapping reagent, the silafulvene undergoes dimerization.

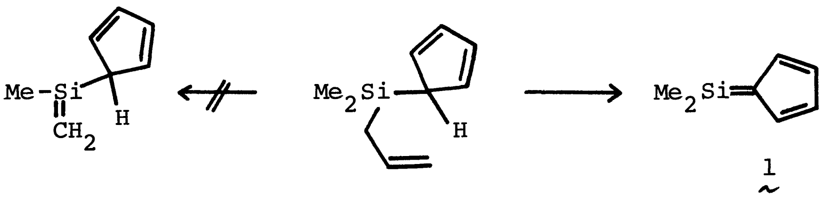
The thermally induced retro ene reaction has been applied successfully to generating silicon-carbon double bonded species such as silabenzenes,[2] 1-silacyclopenta-1,3-diene,[3] and 1-silabuta-1,3-diene.[4] These reactive molecules give usually stable end products by dimerization, rearrangement and reactions with trapping reagents.

We now report generation and some reactions of 6,6-dimethyl-6-silafulvene (1). A CNDO/2 study[5] has predicted an interesting property of 1, but to our knowledge, no report on the generation of 1 has been published to date.

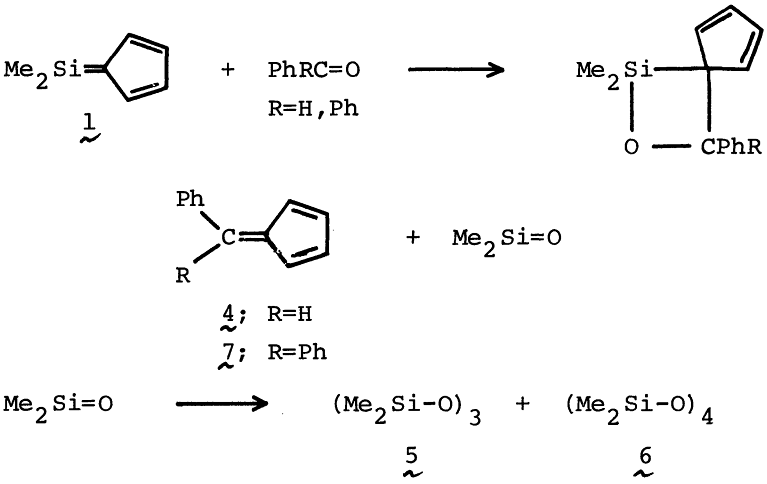
The vacuum-flow co-pyrolysis of (allyl)(cyclopentadienyl)dimethylsilane (2)[6], prepared by the reaction of chloro(cyclopentadienyl)dimethylsilane and allylmagnesium chloride, with methanol through a quartz tube heated at 620°C afforded a 18% yield of (cyclopentadienyl)(methoxy)dimethylsilane (3a)[7] together with recovered 2 (71%). The formation of 3a indicates the generation of 1 by the retro ene reaction. This was further substantiated by a similar trapping experiment with methanol-d_1. Thus, the reaction of 2 with MeOD gave monodeuterated (cyclopentadienyl)(methoxy)dimethylsilane (3b). In the mass spectra of 3b, the parent peak, M^+, appeared at m/e 155 (16.4%) with over 96% isotopic content. It is interesting to note that fragments



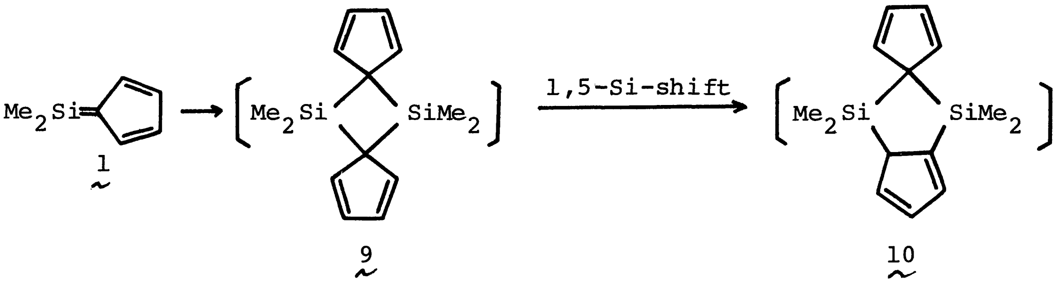
with a cyclopentadienyl group (Cp) such as Me(MeO)CpSi$^+$ (m/e 140, 31.9%) and Me(H)-CpSi$^+$ (m/e 110, 12.3%) contain always deuterium, whereas those without a cyclopentadienyl group such as Me$_2$(MeO)Si$^+$ (m/e 89, 100%) and Me$_2$SiH$^+$ (m/e 59, 25.8%) have no deuterium. These facts demonstrate that the retro ene reaction of 2 occurred only in the direction to form 1 which was successfully trapped by methanol.

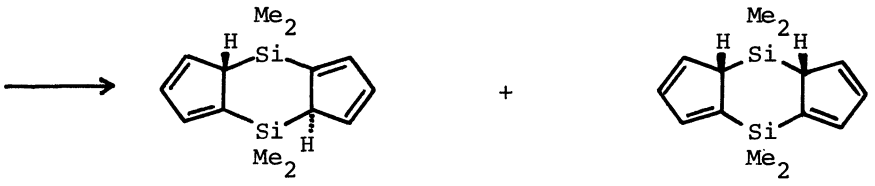


The vacuum-flow co-pyrolysis of 2 with benzaldehyde gave 6-phenylfulvene (4)[8] in 47% yield (after purification with TLC) together with cyclic oligomers of polydimethylsiloxane, 5 and 6. The formation of 5 and 6, evidenced by the GC-MS analysis of the pyrolysate, indicates 6-silafulvene as an intermediate in the reaction.[9] Similarly, a benzene solution of 2 containing benzophenone was subjected to the flow pyrolysis through a quartz tube packed with quartz chips at 600°C to afford 6,6-diphenylfulvene (7)[8] in 28% yield together with cyclic polydimethylsiloxanes, 5 and 6. It is well documented that a silaethene derivative reacts with a carbonyl compound to give a silaoxetane which decomposes to an olefin and a silanone.[10] The latter is known to give 5 and 6. Therefore, these products are best explained by the following scheme of reactions.



The vacuum-flow pyrolysis of 2 at 650°C in the absence of a trapping reagnet yielded a mixture of dimeric products (8a and 8b) of 1 in a 3:1 ratio in 60% yield.

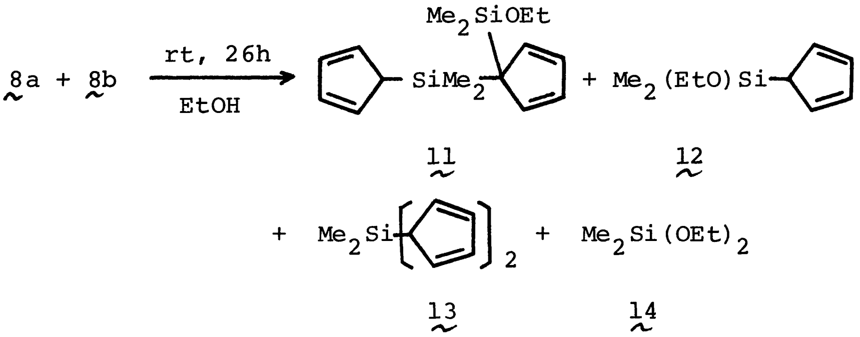




8a **8b**

Giving only one peak on both GLC and HPLC as far as we have examined, the mixture was not separated to each isomer.[11] However, ^{1}H NMR data[12] indicates clearly the structures of the abundant (**8a**) and less abundant (**8b**) isomers to be those indicated above. Thus, **8a** shows two types of SiMe signals (δ -0.49 and 0.53) in an equal intensity together with the 2H peak assignable to that of the allylic hydrogen (δ 3.52), while four types of Si-Me signals (δ -1.38, 0.32, 0.47 and 0.51), accompanied by the resonance (δ 3.81) due to the corresponding allylic hydrogen, are observed for **8b**. The anomalous up-field shift of one of the SiMe signals in **8b** can be rationalized by diamagnetic shielding caused by the two cyclopentadienyl rings of a sandwich like arrangement. In the mass spectrum, the mixture shows a molecular ion at m/e 244 but lacks the peak at m/e 122 which corresponds to the monomeric structure.

Furthermore, the following chemical transformation supports the structures. Thus, ethanolysis of the mixture of **8a** and **8b** gave **11** (38%),[13] **12** (19%),[14] **13** (15%)[15] and **14** (11%).[16]



The mechanism of the formation of **8a** and **8b** is not always clear. However, it is known that silaethene dimerizes rapidly to 1,3-disilacyclobutane[10] and 1,5-silicon shift occurs rapidly in a silylcyclopentadiene system.[17] Therefore, the possible route to the products from **1** may be one shown above in which a 1,3-disilacyclobutane (**9**) is a key intermediate. The stereochemical consequence of the dimers is of considerable interest and we will discuss the matter in a forthcoming paper.

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References and Notes

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6 2; bp 31.5∿33°C/0.6mmHg; ^1H NMR (δ in CCl_4) -0.05 (6H, s, $Si\text{-}CH_3$), 1.56 (2H, d, J=8.1Hz, $Si\text{-}CH_2$), 3.02 (1H, bs, SiCH) 4.79∿5.02 (2H, m, $Si\text{-}CH_2\text{-}CH{=}\underline{CH_2}$), 5.53∿6.10 (1H, m, $Si\text{-}CH_2\text{-}\underline{CH}{=}$) 6.55 (4H, bs, Cp-H); MS m/e (%) M^+ 164 (6.7), 123 (100), 99 (10.0), 95 (22.3). Preparation of 2 has been described by L. N. Maksimova, V. I. Koshutin and V. A. Smironov, Zh. Obshch. Khim., 43, 1198 (1973); Chem. Abst., 79, 53434 (1973).

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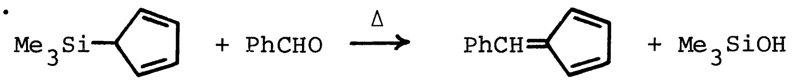
9 As a member of cyclopentadienylmetals, cyclopentadienylsilane reacts with carbonyl compounds to afford a fulvene derivative, as shown typically in the following equation.



However, in this case, no 5 nor 6 can be detected in the product.

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11 8a+8b; mp 108∿109°C; MS m/e (%), M^+ 244 (54), 229 (100). High resolution MS, $C_{14}H_{20}Si_2$ calcd.: 244.1104. Found: 244.1110.

12 8a; ^1H NMR (δ in $CDCl_3$) -0.49 (6H, s, SiMe), 0.53 (6H, s, SiMe), 3.52 (2H, bs, HC-), 6.56∿6.98 (6H, m, HC=). 8b; ^1H NMR (δ in $CDCl_3$) -1.38 (3H, s, SiMe), 0.32 (3H, s, SiMe), 0.47 (3H, s, SiMe), 0.51 (3H, s, SiMe), 3.81 (2H, bs, HC-), 6.56∿6.98 (6H, m, HC=).

13 11; purified by means of preparative VPC. ^1H nmr spectrum is rather complicated due to its fluxional structure. MS m/e (%) M^+ 290 (3.7), 261 (16.7, M-29), 225 (53.9, M-65(Cp)), 123 (100, Me_2SiCp). High resolution MS, $C_{16}H_{26}OSi$ calcd.: 290.1523. Found: 290.1523.

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