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**Supplementary Material Available:** Listings of atomic coordinates, standard deviations, and temperature factors for structures **4** and **5** (53 pages). Ordering information is given on any current masterhead page.

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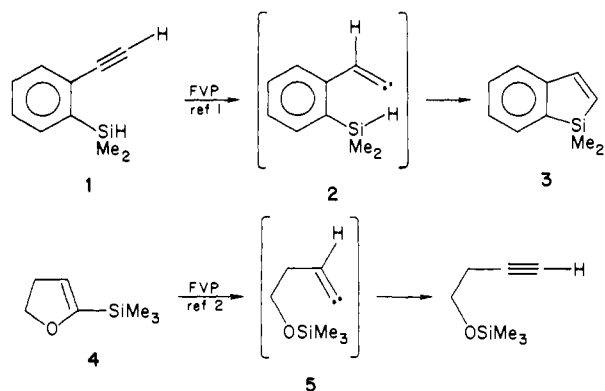
### Thermal Extrusion of Dimethylsilanone from (Hydridosilyl)ketenes. A Retro-Wolff Rearrangement?

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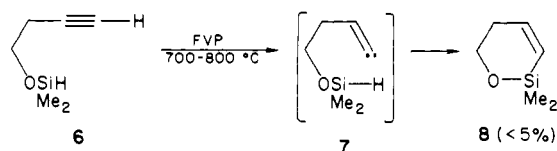
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Recently we reported that the Si-H bond serves as an efficient intramolecular trap for a vinylidene **2**, produced by thermal isomerization of arylacetylene **1**, to afford in high yield silaindene **3**.<sup>1</sup> As we have also discovered that vinylidenes can be produced by reductive elimination in the flash vacuum pyrolysis (FVP) of  $\alpha$ -silyl cyclic enol ethers (e.g., **4**  $\rightarrow$  **5**),<sup>2</sup> we thought to couple these



two reactions to provide a novel and convenient route to dihydrosilapyrans which were needed for another study.

The reductive elimination approach to the desired vinylidene for dihydrosilapyran synthesis was prompted by the failure of acetylene **6** to serve as a dihydrosilapyran precursor. It was hoped that **6** would thermally isomerize to vinylidene **7** and cyclize to dihydropyran **8**. However, FVP of **6**<sup>3</sup> at 700 °C produced only



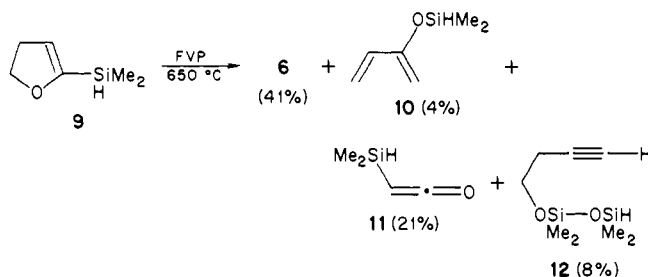
(1) Barton, T. J.; Groh, B. L. *Organometallics* **1985**, *4*, 575.

(2) Barton, T. J.; Groh, B. L. *J. Org. Chem.* **1985**, *50*, 158.

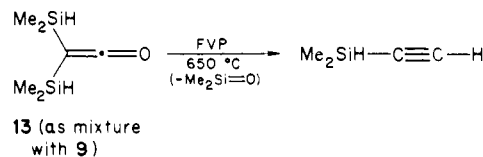
(3) Mironov, V. F.; Kozlikov, V. L.; Fedotov, N. S. *Zh. Obshch. Khim.* **1966**, *39*, 966.

a trace (ca. 5%) of **8**<sup>4</sup> with very little decomposition of **6**. Although major decomposition occurred at 800 °C, there was no improvement in the yield of **8**, and numerous products were formed in very low yields.

Thus, we turned to the reductive elimination route to vinylidene **7** using  $\alpha$ -(dimethylsilyl)dihydrofuran (**9**)<sup>5</sup> as its precursor. FVP of **9** at 650 °C produced no evidence of silapyran **8** although the intermediacy of vinylidene **7** was clearly established through the formation of acetylene **6** (41%). Formation of 2-siloxy-1,3-butadiene (**10**, 4%)<sup>4</sup> and (dimethylsilyl)ketene (**11**, 21%)<sup>4</sup> was preceded from the pyrolysis of **4**.<sup>2</sup> The only surprising product was disiloxane **12**<sup>4</sup> whose presence strongly suggested the intermediacy of dimethylsilanone,  $\text{Me}_2\text{Si}=\text{O}$ . The well-precedented<sup>6</sup> insertion of  $\text{Me}_2\text{Si}=\text{O}$  into the Si-O bond of **6** is the most likely origin of disiloxane **12**.



As the pyrolysis of **6** was already established as not being the source of **12**, the only candidate appeared to be silylketene **11**. Although **11** would appear to be a most unlikely precursor to  $\text{Me}_2\text{Si}=\text{O}$ , this possibility was experimentally explored. Silylketene **11** proved to be too unstable and/or reactive for convenient isolation or handling. Thus, an inseparable mixture of **9** and bis(dimethylsilyl)ketene (**13**)<sup>4,7</sup> (73:27) was copolyzed and found to produce (dimethylsilyl)acetylene, the expected product from



extrusion of  $\text{Me}_2\text{Si}=\text{O}$  from **13**. This acetylene is not formed in the FVP of **9** alone.

Finally, to unambiguously demonstrate that (hydridosilyl)ketenes do indeed thermally decompose by loss of  $\text{Me}_2\text{Si}=\text{O}$  and that only a single hydridosilyl group is required, (trimethylsilyl)(dimethylsilyl)ketene (**14**)<sup>4</sup> was synthesized<sup>8</sup> and pyrolyzed.

(4) Compounds **9**, **12**, and **14** were completely characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and combustion analysis. Compounds **10**, **11**, and **13** were characterized only by spectral means due to insufficient sample, instability, and separation difficulty, respectively. Compound **8** was identified by GC-MS and <sup>1</sup>H NMR comparison with an authentic sample.

(5) Lukevics, E.; Gevorgyan, V. N.; Rozite, S.; Gavars, M.; Mazeika, I. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1984**, (1), 109.<sup>4</sup>

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(7) The surprising formation of ketene **13** during the synthesis of **9** is the subject of a separate paper currently submitted for publication.

(8) Synthesis of **14** was serendipitously accomplished by the method of Pirrung and Hwu<sup>9</sup> through dehydrohalogenation of 1-bromo-2-(trimethylsilyloxy)ethene with LDA. Quenching of the resulting anion with  $\text{Me}_2\text{SiHCl}$  and workup involving distillation (maximum temperature 125 °C), heating with MeI to remove *t*-Pr<sub>2</sub>SiMe<sub>2</sub> (sealed tube, 70 °C, 14 h), and preparative GC provided **14** (11%) instead of the expected<sup>9</sup>  $\text{Me}_2\text{HSiC}\equiv\text{COSiMe}_3$ . Spectral distinction is from the observation of the expected<sup>10-12</sup> ketene bond at 2077 cm<sup>-1</sup>, absence of the acetylenic stretch in the region of 2250 cm<sup>-1</sup>,<sup>11</sup> and the unique silylketene <sup>13</sup>C NMR spectrum [ $\delta$  166.58 (SiC $\equiv$ ), 0.97 (MeSi), -1.34 (MeSi), -1.53 (C=C=O)]. For comparison, the unsaturated carbons of  $\text{Me}_2\text{SiHC}=\text{C}=\text{O}$  and  $(\text{Me}_2\text{Si})_2\text{C}=\text{C}=\text{O}$  absorb at  $\delta$  179, -0.1 and  $\delta$  166.8, 1.7.<sup>13</sup> We are actively studying this problem and will report our findings at a later date.

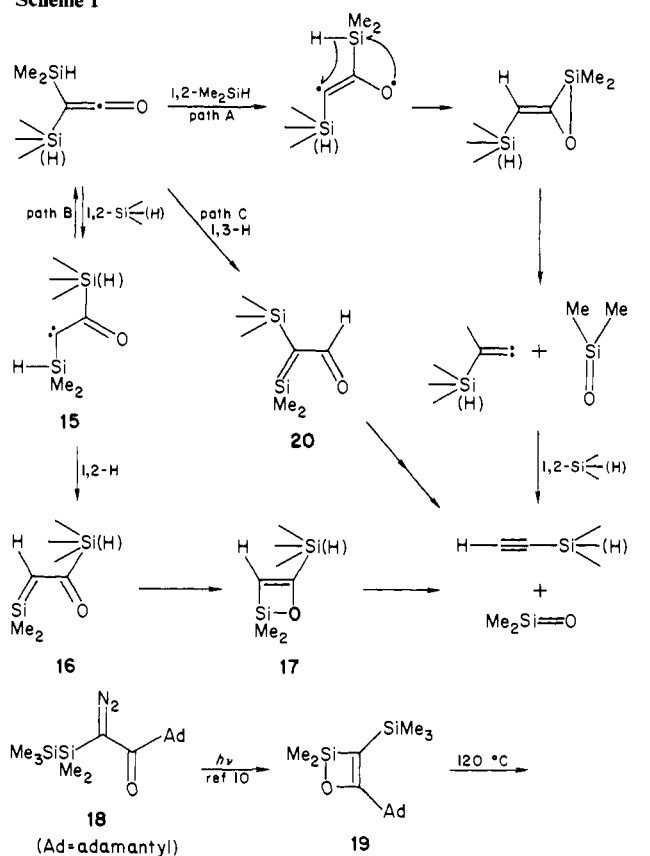
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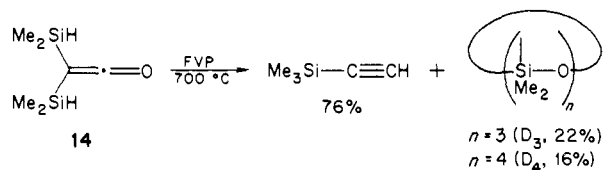
(11) Maas, G.; Brückman, R. *J. Org. Chem.* **1985**, *50*, 2801.

(12) Shchukovskaya, L. L.; Kol'tsov, A. I.; Lazarev, A. N.; Pal'chik, R. *I. Dokl. Akad. Nauk SSSR* **1968**, *179*, 892.

Scheme I



FVP of **14** at 700 °C (67% completion) afforded (trimethylsilyl)acetylene in 76% yield along with permethylcyclotrisiloxane ( $D_3$ , 22%) and permethylcyclotetrasiloxane ( $D_4$ , 16%), the usual



products from oligomerization of  $\text{Me}_2\text{Si}=\text{O}$ . Thus, it is clearly established that hydrosilylketenes thermally decompose by extrusion of silanone.

As to how (hydrosilyl)ketenes thermally extrude silanones, we can offer two mechanistic possibilities (Scheme I) which originate with a 1,2-shift to the central carbon of the ketene to produce a diradical which may be viewed as an  $\alpha$ -keto carbene (**15**). Although the oxasilacyclopropane ring system is known,<sup>14</sup> we tend to disfavor path A largely due to the excellent precedents for each of the proposed steps from **15** to dimethylsilanone in path B. Ando has reported<sup>15</sup> that a disilanyl analogue of **15**, photochemically generated from the corresponding diazo ketone **18**, rearranges by a similar route to afford an isolable silaoxetene, **19**, which extrudes  $\text{Me}_2\text{Si}=\text{O}$  at 120 °C (Scheme I, bottom equation).

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Without question, the most exciting aspect of the decomposition of (hydrosilyl)ketenes is that the first step appears to correspond to what is, to our knowledge, the first example of a retro-Wolff rearrangement. As such, two key factors attributable to silicon are involved in promoting the rearrangement—the superb migratory characteristics of silyl groups<sup>16</sup> and the excellent carbene trapping ability of the Si–H bond. Conversion of **15** to **16** via a 1,2-shift is well preceded on both experimental<sup>17</sup> and theoretical grounds,<sup>18</sup> while the reaction of silenes and ketenes (**16** → **17**) is one of the first silene reactions discovered.<sup>19</sup> However, definite invocation of a retro-Wolff rearrangement must be tempered by recognition that isomerization of the silylketene to **20**, a positional isomer of silene **16**, could occur via a single, unprecedented 1,3-H shift from silicon to carbon (Scheme I, path C).<sup>20</sup> Studies are currently in progress to make more subtle distinctions between paths A, B, and C and to probe more subtle questions such as the possible involvement of oxirene intermediates.

**Acknowledgment.** The support of this work by the National Science Foundation is gratefully acknowledged.

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(20) The high yield of  $\text{Me}_3\text{SiC}\equiv\text{CH}$  in the FVP of **14** is in keeping either with a reversible retro-Wolff rearrangement (path B) or the 1,3-H shift of path C.

## Layer Cross-Linking in Pillared Clays

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Recent <sup>29</sup>Si and <sup>27</sup>Al magic angle spinning (MAS) NMR studies by Plee et al.<sup>1</sup> have indicated that two mechanisms operate for the pillaring of smectite clays by polyoxoaluminum oligomers. For pillared montmorillonite and Laponite (Laporte, Ltd.), the layers retained their constitution even after calcination at 350 °C. However, for calcined pillared beidellite, the tetrahedral sheets of the layers reacted chemically with the gallery oligomers. It was concluded that layer reactivity is dependent on the origin of layer charge (octahedral layer charge for montmorillonite and Laponite, tetrahedral layer charge for beidellite<sup>2</sup>).

Our own <sup>29</sup>Si and <sup>27</sup>Al MAS NMR results for alumina pillared clays confirm the existence of two mechanisms for the pillaring of smectite clays. However, our results also show that the mechanisms are not differentiated solely on the basis of the origin of layer charge. Although calcined alumina pillared montmorillonite and Laponite exhibit no evidence for layer reaction, we

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(2) In octahedrally charged clays such as montmorillonite and Laponite with typical unit cell formulas of  $\text{M}_{0.7/n}^{n+}[\text{Mg}_{0.7}\text{Al}_{1.3}]\text{Si}_{1.0}\text{O}_{20}(\text{OH})_4$  and  $\text{M}_{0.4/n}^{n+}[\text{Li}_{0.4}\text{Mg}_{5.6}]\text{Si}_{1.0}\text{O}_{20}(\text{OH})_4$ , respectively, the layer charge results from metal ion substitutions in the octahedral sheet (e.g., Mg replacing Al or Li replacing Mg). For a tetrahedrally charged clay like beidellite,  $\text{M}_{0.9/n}^{n+}[\text{Al}_{4.0}]\text{Si}_{7.1}\text{Al}_{0.9}\text{O}_{20}(\text{OH})_4$ , the layer charge results from ion substitutions in the tetrahedral sheet (e.g., Al replacing Si).