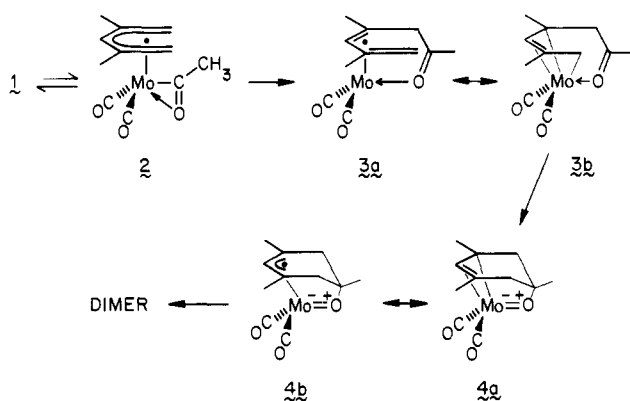


Scheme I



lead to a 16-electron configuration, it would seem likely that other interactions could be present. In this regard, one can note that the separation between molybdenum atoms is 3.215 (1) Å, comparable to the value of 3.235 (1) Å observed in  $[(C_5H_5)Mo(CO)_3]_2$ <sup>7</sup> but much longer than the value of 2.448 (1) Å in  $[(C_5H_5)Mo(CO)_2]_2$ .<sup>8</sup> The Mo–O–Mo angles are rather large compared to the O–Mo–O angles (102.0 (2)° vs. 71.6 (1)°), leading to an extremely short O–O separation of 2.421 Å, which suggests little metal–metal bonding (cf., 1b). However, the sums of the three bond angles about the oxygen atoms average 116.3°, close to that expected for  $sp^2$  hybridization. It would therefore seem likely that 18-electron configurations are reached through  $\pi$  interactions with the oxygen atoms (1c).

Particularly remarkable about this complex, however, is the multistep coupling process that has taken place, during which one carbonyl ligand is converted to an alkoxide.<sup>9</sup> To our knowledge this represents a very new mode of reactivity for a transition-metal carbonyl complex. While it was recognized that subsequent coordination of additional ligands to an actual  $Mo(2,4-C_7H_{11})(CO)_3(CH_3)$  complex might bring about a coupling reaction, it was a surprise to find that such events would take place spontaneously and particularly that the acyl group would couple to *both* ends of the pentadienyl group. A possible mechanism for this process is set out in Scheme I. While most steps have precedent,<sup>6,10</sup> the final coupling process (3 → 4a) is unusual. By utilizing an alternative representation for metal–butadiene bonding (3b), however, one can regard this as an intramolecular alkylation of a coordinated ketone.<sup>11</sup> That a similar cyclization process is not commonly (if ever) observed for related allyl and butadiene compounds might reflect the greater strain in the expected smaller ring products. It may also be noted that the overall reaction bears some similarity to the hydrogenation of CO in the methanol synthesis except that the former reaction is stoichiometric and involves the transfer of alkyl groups, rather than hydrogen atoms, to the carbonyl carbon atoms. In addition, there is some resemblance to the formation of metal–enediolates in various metal carbonyl reactions.<sup>12</sup>

It appears that the coupling chemistry of transition-metal-pentadienyl compounds will prove to be very versatile. Almost certainly the rather unique aspects will lead to useful applications.<sup>13</sup>

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and one can note in particular that the combination of five-membered and single-membered fragments into six-membered rings is an uncommon synthetic strategy. We have, in addition, observed a number of coupling reactions involving other unsaturated organic molecules with metal–pentadienyl compounds,<sup>14</sup> and we are pursuing in greater detail this chemistry and its potential applications.

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**Supplementary Material Available:** Listing of the positional parameters for the non-hydrogen atoms of the molybdenum compound, a table of bond distances and angles, and a structure factor table (14 pages). Ordering information is given on any current masthead page.

(13) (a) In other applications, pentadienylsilanes<sup>13b</sup> and anions<sup>13c</sup> have been employed for pentadienylations, while pentadienylnickel compounds undergo limited coupling reactions.<sup>13d</sup> Cyclohexadienylmetal compounds have a number of useful applications.<sup>13e,f</sup> (b) Seyferth, D.; Pornet, J.; Weinstein, R. M. *Organometallics* **1982**, *1*, 1651. (c) Gerard, F.; Miginiac, P. *Bull. Soc. Chim. Fr.* **1974**, 1924, 2527. (d) Hegedus, L. S.; Varapath, S. *Organometallics* **1982**, *1*, 259. (e) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463 and references therein. (f) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

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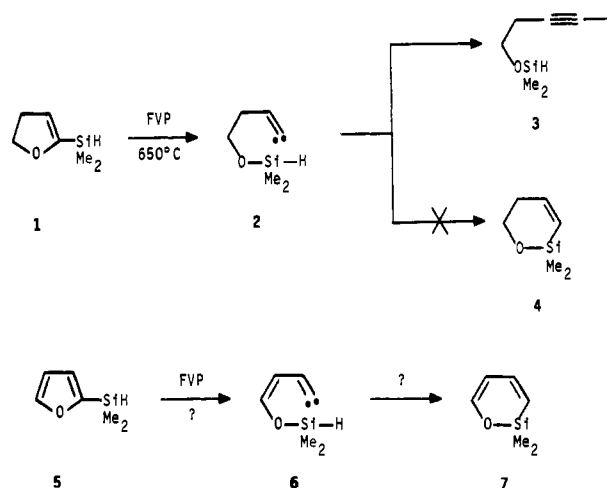
## Silapyran and Silacyclobutene Formation in the Gas-Phase Pyrolysis of 2-(Dimethylsilyl)furan

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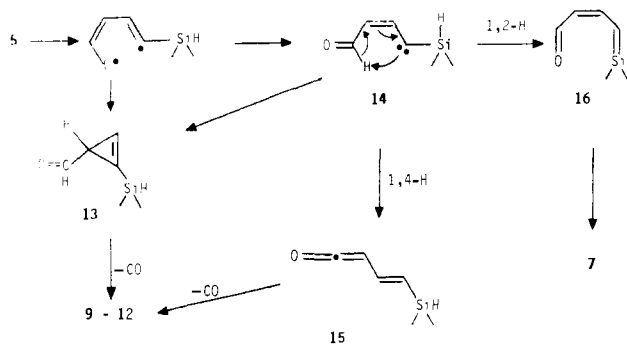
Recently we have reported<sup>1</sup> that flash vacuum pyrolysis of  $\alpha$ -silyl enol ethers provides a route to vinylidenes via reductive elimination of an alkoxy silane. We have also reported<sup>2</sup> a single attempt to utilize this reaction with a cyclic enol ether **1** as a method of ring expansion, but the resulting vinylidene **2** exclusively preferred to collapse to acetylene **3** rather than undergo Si–H insertion to yield **4**. However, it was hoped that greater rigidity



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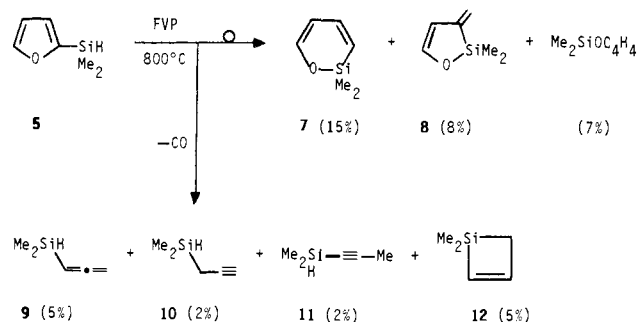
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Scheme I



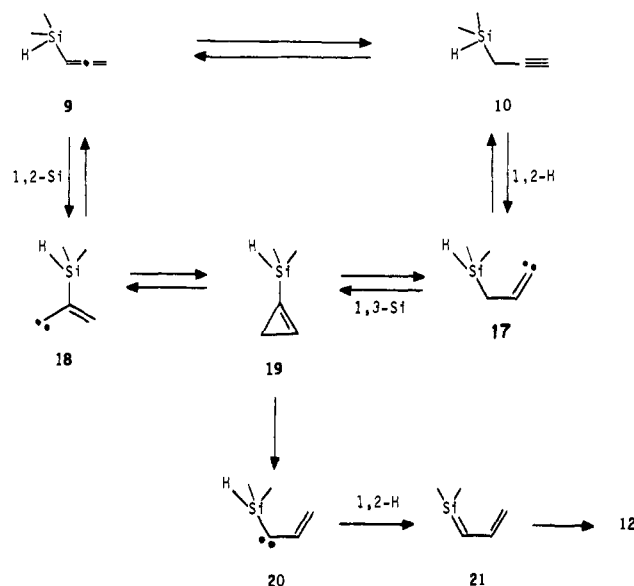
of the vinylidene **6** produced from rearrangement of 2-(dimethylsilyl)furan (**5**)<sup>3</sup> would reduce the entropic requirements (relative to **2**) for cyclization via Si-H insertion.

At 800 °C, the FVP of furan **5** afforded in 15% yield silapyran **7** which was identified by comparison of its spectral features with those of an authentic sample.<sup>4,5</sup> Separation of **7** from the product mixture is greatly complicated by the presence of **5** (15%), isomer **8** (8%),<sup>6</sup> and an unidentified isomer (7%). Also formed in the FVP of **5** were four isomers of Me<sub>2</sub>SiC<sub>3</sub>H<sub>4</sub>, **9**–**12**,<sup>7</sup> corresponding to decarbonylation of **5**. Loss of CO from **5** was not unanticipated as furan is known<sup>8</sup> to decompose to propyne and allene, but the formation of 3,3-dimethyl-3-silacyclobut-1-ene (**12**)<sup>7</sup> was a complete surprise.



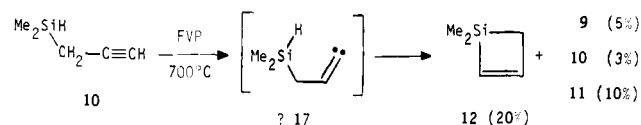
Mechanistic aspects of furan decarbonylation have not been studied, but presumably the process is initiated by C–O homolysis (Scheme I). Closure<sup>9</sup> of the resulting diradical to acylcyclopropene **13** would provide a system capable of decarbonylation. However, as the thermal decarbonylation of aldehydes is generally more complex<sup>11</sup> than that of ketenes,<sup>12</sup> we favor isomerization to

Scheme II



ketene **15** prior to loss of CO. It is of interest to note that the intermediate vinylcarbene **14** could also serve as a source of silapyran **7** by way of a well-established<sup>13</sup> 1,2-migration of hydrogen to produce silene **16** which should cyclize to **7**. Thus, the formation of **7** in the pyrolysis of furan **5** does not demand the intermediacy of vinylidene **6**.

Probably the most interesting question is that of the origin of 3,3-dimethyl-3-silacyclobut-1-ene (**12**). Silanes **9** and **10** are expected to equilibrate,<sup>14</sup> and we have found that in the case of the trimethylsilyl analogues at higher temperatures this equilibrium is bled to the 1-propynyl isomer—in this case **11**. However, if a silacyclobutene is to originate from this energy surface it must be dependent upon the system possessing an Si–H unit. In order to demonstrate that the origin of **12** is indeed the acetylenic/allenic mixture **9**–**11**, 3-(dimethylsilyl)propyne (**10**) was independently



pyrolyzed. At 700 °C the major constituents of the FVP of **10** were **9** (5%), **10** (3%), **11** (10%), and **12** (20%). Because of the large number of intermediates one can write for a connecting energy surface between isomers **9**–**12** there exist a considerable number of mechanistic possibilities for the formation of a silacyclobutene. The simplest of these is isomerization<sup>12</sup> of **10** to vinylidene **17** followed by intramolecular Si–H insertion. Ultimately, the only hope of significantly narrowing down the mechanistic possibilities will be nontrivial double-labeling experiments.

Lastly, we would comment on the implications of another mechanistic possibility for the formation of **12** (Scheme II). As **10** is in equilibrium with allene **9**, one must consider a route involving 1,2-silyl migration to sequentially produce vinylcarbene **18**, cyclopropene **19**, and vinylcarbene **20**. This latter intermediate would be expected<sup>13</sup> to isomerize to vinylsilene **21**, a system that is known<sup>15</sup> to close to **12**. Such a pathway is supported by recent ab initio calculations on allene–propyne isomerization.<sup>16</sup> The (trimethylsilyl)allene–propargylsilane isomerization has been the subject of extensive kinetic and stereochemical investigation<sup>14</sup> and

(3) Prepared from  $\alpha$ -lithiofuran and Me<sub>2</sub>HSiCl in 47% yield: NMR (CCl<sub>4</sub>)  $\delta$  0.35 (d, 6 H,  $J = 6$  Hz), 4.45 (SiH, hep,  $J = 6$  Hz), 6.30 (d, of d, 1 H,  $J = 2, 3$  Hz), 6.59 (d, 1 H,  $J = 3$  Hz), 7.55 (d, 1 H,  $J = 2$  Hz); mass spectrum,  $m/e$  (% relative intensity) 126 (18), 125 (6), 111 (100), 85 (33);  $\lambda_{\text{max}}^{\text{MeCN}}$  244 (10022). Hussmann, G. P. Ph.D. Dissertation, Iowa State University, Ames, IA, 1983.

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has always been presented<sup>14,17</sup> as a concerted 1,3-migration of silicon. We are not of that view and believe that the path is similar to that found for the C<sub>3</sub>H<sub>4</sub> surface<sup>16</sup> involving vinylcarbene, cyclopropene, and vinylidene intermediates as shown in Scheme II. Thus, the observed stereochemical outcome of inversion on silicon<sup>14</sup> is accommodated by a 1,2-Si migration with retention followed by a 1,3-Si migration with inversion. Further studies are currently in progress on the mechanistic details of silyllallene isomerizations.

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

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## Gas-Phase Generation of Singlet Oxygen by Reaction of Ozone with Organic Substances

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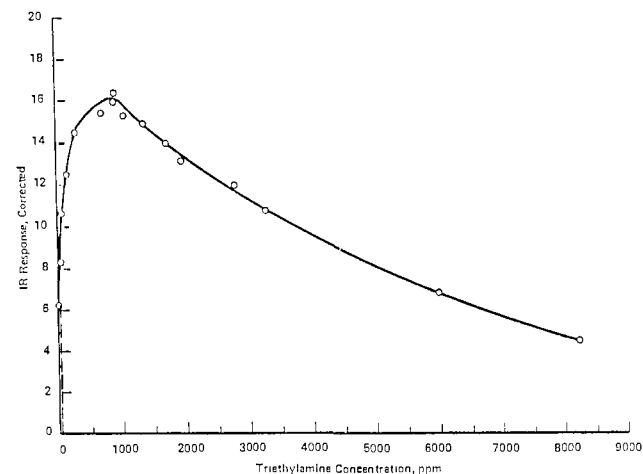
The reaction of ozone (O<sub>3</sub>) with organic substances in the gas phase has been studied extensively because of the presence of ozone in the atmosphere.<sup>1</sup> One of us<sup>2</sup> has suggested that some ozone reactions occurring in polluted atmospheres may be sources of singlet oxygen. A number of liquid-phase reactions of ozone have been shown to give singlet oxygen.<sup>3</sup> Many of the methods used to gain evidence for singlet oxygen in the solution reactions of ozone are not readily adapted to the gas phase. We now report that we have used the 1.27-μm emission of O<sub>2</sub>(<sup>1</sup>Δg) to gain evidence for the formation of singlet oxygen in the gas-phase reactions of ozone with a variety of organic substrates. These reactions are characterized by the transfer of one oxygen atom from ozone to the oxidized substrate concurrent with singlet oxygen production.

When oxygen gas containing triethylamine was mixed with oxygen gas containing ozone at atmospheric pressure,<sup>4,5</sup> singlet Δ oxygen was formed as evidenced by observing the 1.27-μm emission.<sup>6,7</sup> A record of the 1.27-μm emission and the quantity

**Table I.** Observed 1.27-μm Emission in the Reaction of Ozone with Organic Substances

reactant	reactant concn, ppm	O <sub>3</sub> concn, ppm	1.27-μm emission, mV	<sup>1</sup> O <sub>2</sub> concn, <sup>a</sup> ppm
bkgd	0	0	0.3	0.000
control 1	297	0	0.3	0.000
control 2	0	2340	0.6	0.003
triethylamine	297	2340	15.0	0.109
diethyl sulfide	366	2290	7.0	0.050
methyl disulfide	337	2370	1.4	0.009
trimethyl phosphite	380	2330	1.6	0.011
triethyl phosphine	381	2330	0.8	0.005
N-methylpiperidine	351	2290	25.4	0.186

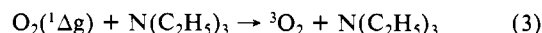
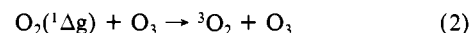
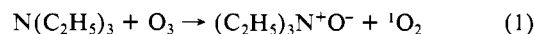
<sup>a</sup> The O<sub>2</sub>(<sup>1</sup>Δg) concentration was established in chemical trapping experiments with 2,3-dimethyl-2-butene and therefore is a minimum concentration.



**Figure 1.** Plot of O<sub>2</sub>(<sup>1</sup>Δg) emission vs. triethylamine concentration at an ozone concentration of ~2350 ppm.

of O<sub>2</sub>(<sup>1</sup>Δg) produced with several substrates is given in Table I. Control experiments in which oxygen containing ozone was passed through the optical detector gave signals near background level. Other control experiments with oxygen containing triethylamine also gave the same result.

Figure 1 is a plot of the 1.27-μm emission vs. triethylamine concentration at an ozone concentration of ~2350 ppm. The observed dependence on N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> can be explained in terms of eq 1-3. Singlet oxygen was generated in the reaction of tri-



ethylamine with ozone (eq 1). Ozone (eq 2)<sup>8</sup> and triethylamine (eq 3)<sup>9</sup> are potent singlet oxygen quenchers and would be expected to remove O<sub>2</sub>(<sup>1</sup>Δg) from the gas phase as seen in Figure 1. The singlet oxygen concentration passes through a maximum at a N(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> concentration that is ~35% of the required stoichiometric amount. This concentration is presumably dictated by the combined influence of eq 1-3. At higher triethylamine concen-

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(4) The experimental apparatus was composed of 1/4-in. stainless steel tubing with valves for flow control and dilution. Ozone was generated by passing oxygen (99.995%) through a Welsbach generator. Oxygen gas streams containing the organic substrates were generated by passing oxygen (99.995%) through a bubbler containing the liquid organic substrate.

(5) The concentration of the organic substrate in the gas phase was monitored by using gas chromatography with flame ionization detection. A Dasibi monitor was used to measure the ozone concentration.