

responding barbaralyl sulfate VIII. When sulfate VIII-9-*d* was treated with EtSK/EtSH in THF at 20 °C for 3 days, a 1:1 mixture of sulfide IV-*d* and 9-deuteriobarbaralyl ethyl sulfide (V-9-*d*) was obtained in low yield. If the solution was refluxed, the ratio changed to 1:6 favoring V. The sulfate VIII reacted very sluggishly in DMF at 70 °C with NaN<sub>3</sub> to give a 3:22 mixture of azides VI and VII. Since solvolysis of 9-deuteriobarbaralyl tosylate was reported to give only barbaralyl products,<sup>17</sup> the formation of bicyclononatrienyl sulfide IV-*d* and azide VI-*d* underscores the existence of a previously undetected reaction pathway. Since the same labeling pattern was observed in sulfide IV-*d*, formed from sulfates III-2-*d* and VIII-9-*d*, both sulfates probably reacted via the same intermediate.

We propose that the bicyclononatrienyl products obtained from either sulfate III or VIII are the result of nucleophilic capture of the totally degenerate bicyclononatrienyl radical I.<sup>18</sup> To date, we have found that only polarizable, easily oxidized nucleophiles react with sulfates III and VIII to generate radical I. As the ionization potential of the nucleophile increases, a cationic pathway becomes increasingly competitive with electron transfer. The products observed are in accord with this analysis. EtSK reacts only by electron transfer, whereas the higher ionization potential of NaN<sub>3</sub> results in both pathways being competitive. Substitution of an even less easily oxidized nucleophile such as KOAc/18-crown-6 ether or KOH leads to exclusive formation of barbaralyl products.

The nature of the chemical bonding of the bicyclononatrienyl radical is intriguing since the radical may be delocalized in the same sense as was suggested for the bicycloaromatic bicyclononatrienyl anion.<sup>21</sup> To date, such nonclassical radicals are unknown.<sup>22,23</sup> Experiments are currently underway to elucidate this matter as well as to determine the generality of the reaction pathway for other appropriate systems.

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- The choice of the nucleophilic group was quite limited since the propensity of the bicyclononatrienyl derivatives to isomerize to the barbaralyl counterpart precluded the preparation of more reactive derivatives. When bicyclononatrienyl *p*-nitrobenzoate or dinitrobenzoate was substituted for sulfate III, the addition of KSET, NaN<sub>3</sub>, or KOAc/18-crown-6 ether generated a blue-colored solution (presumed to be a charge-transfer or Meisenheimer complex) which, upon workup, gave only starting material.
- <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.28 (t, 3 H, *J* = 8 Hz), 2.63 (q, 2 H, *J* = 8 Hz), 3.25 (m, 3 H), 4.93 (d of m, 1 H, *J* = 5 Hz), 6.15 (m, 3 H), 6.6 ("t", 2 H, *J* = 7 Hz); mass spectrum *m/e* 178, 149, 117, 115 (base).
- <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.20 (t, 3 H, *J* = 8 Hz), 2.5 (m, 5 H), 4.0 (m, 4 H), 5.6 (m, 2 H); mass spectrum of V-9-*d* *m/e* 179, 150, 118, 116 (base).
- Controls revealed that sulfides IV and V do not interconvert at 70 °C. Likewise azides VI and VII are also stable under the reaction conditions.
- <sup>1</sup>H NMR (270 MHz) (CDCl<sub>3</sub>) δ 3.32 (m, 1 H), 3.50 (m, 1 H), 3.73 (m, 1 H), 5.02 (m, 1 H), 6.27 (m, 3 H), 6.79 (m, 2 H); mass spectrum *m/e* 131 (p - N<sub>2</sub>), 130 (base); IR 4.8 μ.
- <sup>1</sup>H NMR (180 MHz) (CDCl<sub>3</sub>) δ 2.64 (m, 2 H), 3.31 (m, 1 H), 4.08 (m, 4 H), 5.57 ("t", 1 H, *J* = 7 Hz), 5.84 ("t", 1 H, *J* = 7 Hz); IR 4.8 μ.
- The apparent low yields reflected the low conversion of sulfate III since, after workup, addition of KOH to the aqueous layer hydrolyzed the residual III to give barbaralol with an overall material balance of 80%.
- At 180 MHz, the multiplet of VII-*d* at δ 4.08 split into two multiplets centered at 3.97 and 4.19, corresponding to H<sub>6</sub> and H<sub>8</sub> (anti to the azide) and H<sub>2</sub> and H<sub>4</sub> (syn to the azide). The proton assignment assumes that the C<sub>2</sub> and C<sub>4</sub> hydrogens which are syn to the azide will be more deshielded than the C<sub>6</sub>

and C<sub>8</sub> hydrogens. A similar shielding effect has been reported for the 9-barbaralyl *p*-nitrobenzoate-*d*.<sup>5a</sup>

- An identical scrambling of labels has been observed for the 2-deuteriobicyclononatrienyl anion;<sup>18</sup> however, the anion is not a viable intermediate for this reaction. The half-life for the deuterium scrambling of the anion is too long, i.e., 10 min at 28 °C in THF. Moreover, no bicyclononatriene arising from protonation by the ethyl mercaptan was observed.
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- At the present, one cannot state whether electron transfer occurs prior to or subsequent to cleavage of the carbon oxygen bond of sulfates III and VIII. During the reaction of III with EtSK, the catalysis observed from potassium argues for a S<sub>RN</sub>1 pathway (radical chain). The failure to obtain any C<sub>9</sub>H<sub>10</sub> hydrocarbon despite the presence of EtSH suggests a radical-cage mechanism. The insensitivity of the azide product distribution to reaction conditions is inconsistent with a radical-chain pathway. Electron transfer from azide ion would be somewhat surprising since azide ion, unlike thiolate anions, do not engage in S<sub>RN</sub>1 reactions without prior photostimulation or entrainment.<sup>19,20</sup> Preliminary electrochemical data involving irreversible processes indicate that electron transfer from EtSK to sulfate III may be endothermic by ~0.1 V, whereas the same process involving the azide ion is endothermic by ~1.0–1.5 V.
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- See ref 2 and 17 and references therein.
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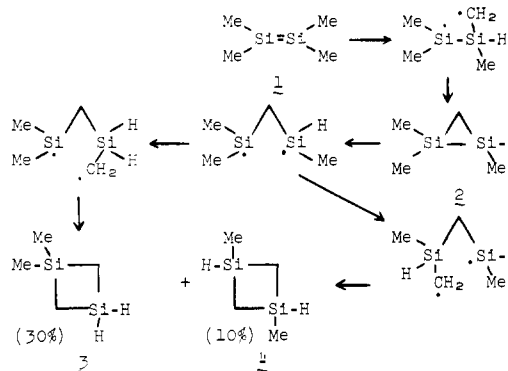
## On the Role of Trimethylsilylmethylsilylene in the Gas-Phase Reactions of Tetramethyldisilene

Sir:

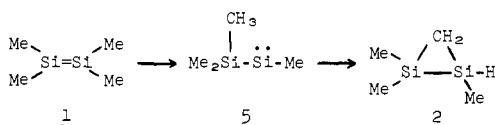
In view of the crescendo of activity in the area of silene (compounds containing a silicon-carbon (p-p) π double bond) chemistry<sup>1</sup> in the past 6 years, the apparent lack of interest in disilenes (compounds with silicon-silicon double bonds) is somewhat surprising. To date the reported reactions of transient tetramethyldisilene (**1**) are restricted to Diels-Alder addition to dienes,<sup>2,4</sup> cycloaddition to an acetylene,<sup>3</sup> addition to benzaldehyde,<sup>4</sup> and an intriguing rearrangement to 1,3-disilacyclobutanes in the gas phase.<sup>2,3,5</sup> This rearrangement, discovered in the pioneering work of Peddle,<sup>2</sup> was proposed to proceed by the mechanism shown in Scheme I.

The key feature of this mechanism is the 1,2 migration of hydrogen from carbon to a silyl radical, which must occur twice to generate the observed major products **3** and **4**. We have never been particularly enamored of this mechanism since it would suggest an inherent instability for any organosilyl

Scheme I

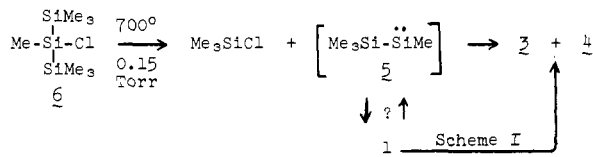


Scheme II

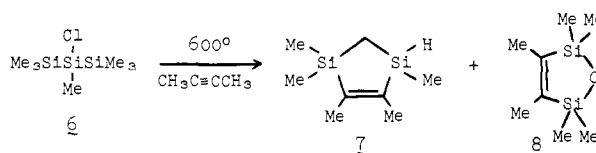


radicals bearing an  $\alpha$  hydrogen, which is not in fact the case.<sup>6</sup> Thus, we wished to examine an alternative scheme in which the initial step is a rearrangement of disilene **1** to trimethylsilylmethylsilylene (**5**), Scheme II. Intramolecular insertion into a methyl C-H bond by the silylene would produce the same intermediate disilacyclopropane **2** found in Scheme I.

Trimethylsilylmethylsilylene (**5**) has not been reported; so it was necessary to generate this silylene to examine its chemistry. This was accomplished through the thermally induced  $\alpha$ -elimination of trimethylchlorosilane from 2-chloroheptamethyltrisilane (**6**). Gas-phase, vacuum-flow pyrolysis of **6** at 700 °C (0.15 Torr) produced disilacyclobutanes **3** and **4** in 28 and 15% yields, respectively.<sup>7</sup>



The obvious question is whether this means that silylene **5** is rearranging to disilene **1** and then proceeding to products through the mechanism in Scheme I, or whether **5** inserts into a C-H bond to afford disilacyclopropane **2** as in Scheme II. Since disilene **1** is known to react with 2-butyne in the gas phase,<sup>3</sup> **6** and 2-butyne were copolyolyzed in a N<sub>2</sub>-flow system at 600 °C to search for disilene products. The major product of this reaction is 1,3-disilacyclopentene (**7**, 23%), and this is also the major product (28%) from gas-phase generation of disilene **1** in the presence of 2-butyne.<sup>3</sup> However, the reaction

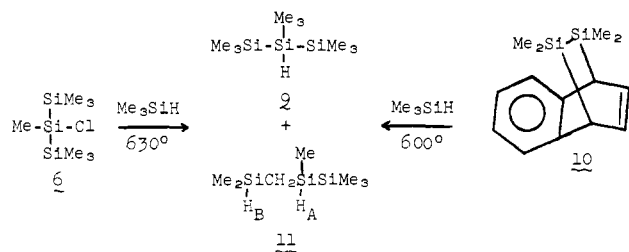


of **1** and 2-butyne also produces a considerable amount (8.5%) of **8** which arises from oxygen insertion<sup>8</sup> into the disilacyclobutene cycloaddition product of **1** and 2-butyne. Siloxane **8** was identified by gas chromatography-mass spectrometry in the product mixture resulting from copolyolysis of **6** and 2-butyne. Although present only in a trace amount (<1%), siloxane **8** does suggest some leakage of **5** to **1**.

Disilene **1** (from **10**)<sup>2</sup> reacts with benzaldehyde in the gas phase to afford *trans*-stilbene (21%), hexamethylcyclotrisiloxane (D<sub>3</sub>, 14%), and octamethylcyclotetrasiloxane (D<sub>4</sub>, 10%). Copolyolysis of trisilane **6** and a tenfold excess of benzaldehyde at 600 °C in a N<sub>2</sub>-flow system also produced *trans*-stilbene<sup>9</sup> (17%), but *none* of the cyclosiloxanes (D<sub>3</sub> or D<sub>4</sub>). Thus, we can find no evidence that **5** rearranges to **1** in this experiment.

It was necessary to consider the possibility that tetramethyldisilene rearranges to silylene **5**. To experimentally check this possibility, an unambiguous trapping reaction for **5** had to be demonstrated. Since the Si-H bond is well known to be a superb trap for silylenes, trisilane **6** was copolyolyzed with an excess of trimethylsilane at 630 °C in a flow system. The expected product, trisilane **9**, was obtained in 10% yield. Copolyolysis of disilene generator **10**<sup>2</sup> with excess trimethylsilane also afforded **9** (17%).<sup>10</sup>

Thus, a strong argument is presented that disilene **1** initially rearranges to silylene **5**, which then proceeds to disilacyclopropane **2** via C-H insertion.<sup>11</sup> The disilacyclopropane can be



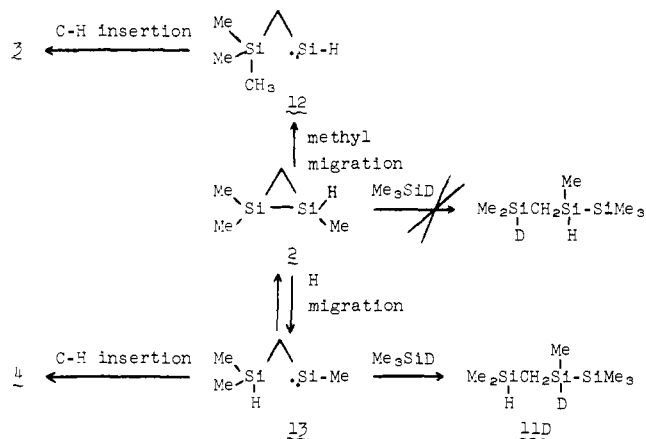
trapped (2-butyne) or, in the absence of trapping agents, continue on to the ultimate products, **3** and **4**. We propose to dispense with the second migration of hydrogen to a silyl radical in Scheme I by having **2** thermally rearrange through  $\alpha$ -eliminations to either silylene **12** (Me migration) or **13** (H migration). Intramolecular C-H insertion by these silylenes would produce the observed products **3** and **4** (Scheme III).<sup>12</sup>

Information on the rearrangement of **2** can be obtained from 2,2,3,5-tetramethyl-2,3,5-trisila-hexane (**11**), which is formed in 17% yield in the copolyolyses of trimethylsilane and both **6** and **10**. This product could arise from either SiH addition across the Si-Si bond of **2** or from Si-H insertion by silylene **13**. That *all* of **11** comes from **13** was established by conducting the copolyolysis of **6** and Me<sub>3</sub>SiD. Product **11D** afforded an NMR spectrum where the silyl hydride sextet of H<sub>A</sub> ( $\delta$  4.01, 1:5:10:10:5:1, both *J*'s = ~5.5 Hz) observed for **11** was absent, but the symmetrical nonet for SiH<sub>B</sub> remained at  $\delta$  4.27.<sup>13</sup>

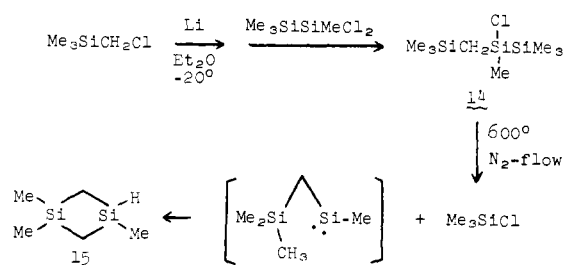
Finally, it was necessary to establish whether or not silylenes like **12** and **13** would in fact undergo this unprecedented intramolecular C-H insertion to afford four-membered rings. To this end disilane **14** was synthesized and subjected to N<sub>2</sub>-flow pyrolysis at 600 °C. The "expected" product 1,1,3-trimethyl-1,3,-disilacyclobutane<sup>5</sup> (**15**) was obtained in 39% yield (Scheme IV).<sup>14</sup>

In summary we conclude that in the gas phase (1) tetramethyldisilene rearranges to trimethylsilylmethylsilylene,<sup>15</sup> (2) silylsilylenes can undergo intramolecular C-H insertion to form disilacyclopropanes,<sup>16</sup> (3) disilacyclopropanes undergo  $\alpha$ -elimination to produce  $\beta$ -silylsilylenes, and (4)  $\beta$ -silylsilylenes

Scheme III



Scheme IV



can undergo intramolecular C-H insertion to afford 1,3-disilacyclobutanes. To our knowledge, even the suggestion of any of these conclusions is unprecedented.

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- All products reported here were established by both their mass spectra and  $^1\text{H}$  NMR spectra. Complete details will be included in the full paper.
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- Discussion of the mechanistic origin of *trans*-stilbene in this reaction will be deferred until the full paper. The yield is based on an assumed 1:1 stoichiometry. We have not yet isolated and identified the products containing silicon and oxygen.
- The yields of **9** and **11** are based on the amount of naphthalene produced in the decomposition.
- Evidence for the generation of a disilacyclopropane in solution from an intramolecular Grignard closure has been reported by D. Seyferth and D. P. Duncan, *J. Organomet. Chem.*, **111**, C21 (1976).
- The obvious problem of the observed relative yields of **3** and **4** and the expected migratory aptitudes of Me and H in **2** can be explained by an equilibrium between **2** and **13**.
- The silyl hydride quartet in the spectrum of **9** ( $\delta$  3.43,  $J = 6$  Hz) also disappeared in this experiment as required.
- Based on reacted **14**, as measured by  $\text{Me}_3\text{SiCl}$  production (47%), the yield of **15** is 83%. However, no **14** was observed by GC in this remarkably clean pyrolysis.
- SCF-MO calculations for the  $\text{Si}_2\text{H}_4$  system presented by Dr. Lawrence C. Snyder at the Pauling Award Symposium, Nov 5, 1977, Eugene, Ore., suggest that this should be exothermic. We thank Dr. Snyder for copies of his slides.
- We are aware that our results for **5** are in striking contrast to those by reported by H. Sakurai,<sup>17</sup> where **5** was found to undergo essentially quantitative dimerization to the corresponding disilene. We must withhold comment on this apparent dichotomous behavior until we can compare the reaction conditions.
- H. Sakurai, the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 14, 1978, ORGN 75.

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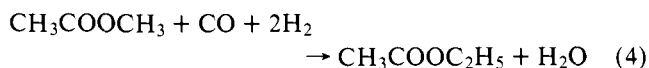
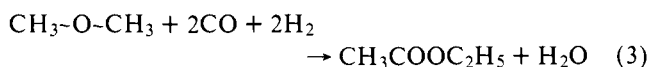
## Simultaneous Carbonylation and Homologation of Dimethyl Ether and Homologation of Methyl Acetate to Ethyl Acetate in the Presence of Ruthenium Catalysts

Sir:

Many cobalt, rhodium, and iridium compounds in conjunction with iodide promoters have been reported to catalyze the homologation of methanol to ethanol<sup>1</sup> or the carbonylation of methanol to acetic acid.<sup>1,2</sup> Ruthenium and osmium halides have been also used as promoters for cobalt/iodide catalysts in the homologation of methanol.<sup>3</sup> It is also known that non-cyclic ethers and esters may undergo carbonylation to give esters (eq 1)<sup>1</sup> and anhydrides (eq 2),<sup>1,4</sup> respectively, in low yields (10–50%).



We wish to report a new possibility of homologation of dimethyl ether and methyl acetate to ethyl acetate (eq 3 and 4).



In the course of studying the homologation of methanol in the presence of some ruthenium catalytic systems with iodide promoters,<sup>5</sup> we found that dimethyl ether and methyl acetate, which, together with ethanol, were the predominant products of the reaction (see Table I, run 1), could be further carbonylated.<sup>6</sup> The catalytic system used was based on ruthenium precursors such as tris(acetylacetonato)ruthenium(III) or diiodotetracarbonylruthenium(II) with iodide promoters ( $\text{CH}_3\text{I}$ , HI, or NaI).

The nature of the products (see Table I) was verified mass spectrometrically while the quantitative data were obtained by GC analysis.<sup>7</sup>

The homologation of dimethyl ether and methyl acetate to ethyl acetate has a selectivity as high as 80%. The reaction can be carried out in toluene or dioxane, the highest yields being observed in acetic acid or, better, acetic anhydride which reduces the hydrolysis of the esters. Even the simple carbonylation of dimethyl ether to methyl acetate according to eq 1 proceeds with the Ru/I catalytic system, especially in hydrocarbons (see Table I, run 2). However, this reaction does not occur with carbon monoxide alone (200 °C (230 atm);  $\text{RuI}_2(\text{CO})_4/\text{HI}$ , 1/10) and a low hydrogen partial pressure of at least 3–5 atm is necessary to initiate the reaction.

Under the reaction conditions, besides simple (eq 1) and reductive carbonylation (eq 3 and 4), hydrolysis, esterification, and transesterification of the products can take place. Starting from dimethyl ether the selectivity to ethyl acetate can be enhanced by using appropriate ratios among the reagents and sufficiently long reaction times to convert the methyl acetate formed. Moreover, the reductive carbonylation increases with respect to the carbonylation alone by increasing the  $\text{H}_2/\text{CO}$  ratio (see Table II). It is also interesting to note that the dimethyl ether homologation, following essentially eq 3 or eq 1 + 4, takes place only when  $\text{CH}_3\text{I}$  is used as promoter. In this case, both new acetyl and ethyl groups were formed (see Table I, runs 3 and 6). In the presence of NaI (see Table I, runs 4 and 7) no formation of new acetyl groups was observed; only a large reductive carbonylation of the methyl to ethyl groups took place, and the acetyl groups of the products clearly originated from acetic acid used as solvent.

The essential requirement of the catalytic system, besides the specific presence of an iodide promoter, was the presence of an acid component such as HI, initially added or formed during the reaction from  $\text{CH}_3\text{I}$ , or an organic one such as acetic acid. The presence of an acid seems to be essential since in the absence of a proton supplier the carbonylation reaction did not proceed.

Contrary to what observed for the rhodium/iodide catalyst,<sup>2</sup> methyl iodide seems not to be involved in the homologation reaction in the presence of ruthenium catalysts. In fact pure  $\text{CH}_3\text{I}$  was not carbonylated or homologated under our reaction conditions but only partially hydrogenated to methane and HI. On the other hand, HI was a promoter more active than  $\text{CH}_3\text{I}$  when used at the same I/Ru ratio.

Some insight into the ruthenium species involved in the catalytic cycle came from the study of the metallic complexes present in the final reaction mixture. Thus, the diethyl ether solution of the catalyst, recovered from the reaction after separation of the excess of NaI, contained a product, not separable in a pure form, in which the Ru/I/Na/CO ratio was 1/3.1/0.99/3.05.<sup>8</sup> The IR spectrum of the product showed  $\nu(\text{CO})$  absorptions at 2114 (s) and 2045 (s)  $\text{cm}^{-1}$  (KBr) compared with the IR absorptions at 2112 (s) and 2051 (vs)  $\text{cm}^{-1}$  (KBr), reported in the literature for  $\text{Cs}[\text{RuI}_3(\text{CO})_3]$ .<sup>9</sup> Reaction of the ether solution with triphenylphosphine gave pure  $\text{RuI}_2(\text{CO})_2(\text{PPh}_3)_2$  as reported by Cleare and Griffith<sup>9</sup>