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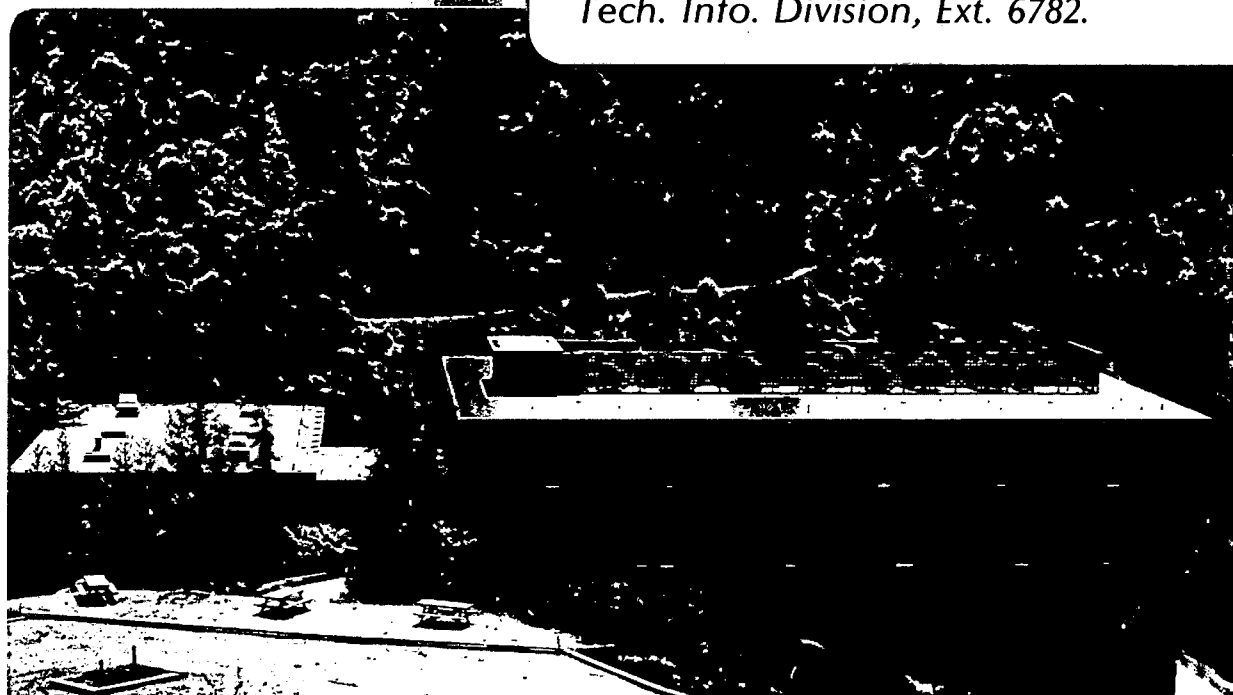
THE SILICON-CARBON DOUBLE BOND: A HEALTHY  
RIVALRY BETWEEN THEORY AND EXPERIMENT

Henry F. Schaefer III

March 1982

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The Silicon-Carbon Double Bond : A Healthy Rivalry  
Between Theory and Experiment

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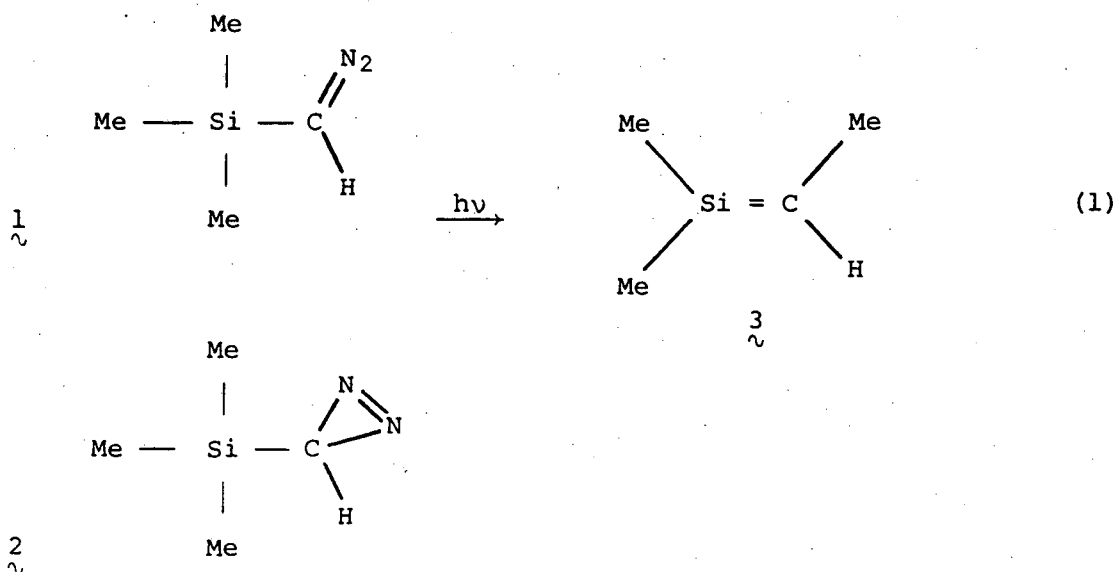
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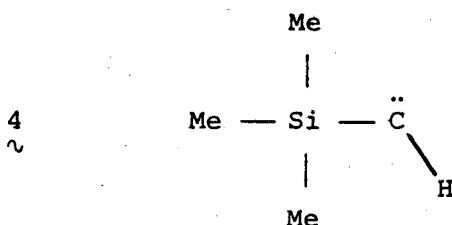
# Introduction

It may be stated with a reasonable level of sobriety that the characterization of silaolefins has become the subject of considerable experimental scrutiny during the past five years.<sup>1-4</sup> This chronological distinction is set by the appearance in late 1976 of back-to-back communications in the Journal of the American Chemical Society by the groups of Chapman and Barton<sup>5</sup> and of Shecter.<sup>6</sup> We concur with the statement of Chapman<sup>5</sup> that this research represented "the first physical and chemical characterization of a silicon-carbon double bond." Moreover the Chapman-Barton-Shecter papers were a milestone comparable to the earlier work of Gusel'nikov<sup>7</sup> (on the pyrolysis of silacyclobutanes) in the ongoing transformation of silaethylenes from "unstable intermediates" to reasonably well understood chemical compounds.

Chapman, Chang, Kolc, Jung, Lowe, Barton, and Tumey<sup>5</sup> found that the irradiation of either trimethylsilyldiazomethane (1) or trimethylsilyldiazirine (2) matrix isolated in argon at 8°K gives rise to 1,1,2-trimethylsilaethylene (3):

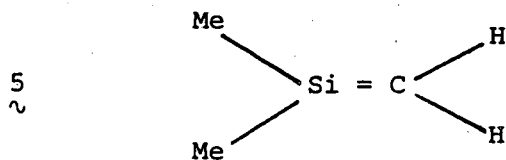


The identity of the silaethylene  $\underset{\sim}{3}$  was established by the thermal dimerization at temperatures above 45°K to form the pertinent disilacyclobutane. Although the infrared spectrum of the trimethylsilaethylene was recorded with great care, it was not possible to assign the Si=C double bond stretching vibration. Chedekel, Skoglund, Kreeger, and Shecter<sup>6</sup> also reported the IR spectrum of  $\underset{\sim}{3}$ , but the more unique aspect of their research was the electron spin resonance spectrum of the triplet ground state of trimethylsilylmethylene



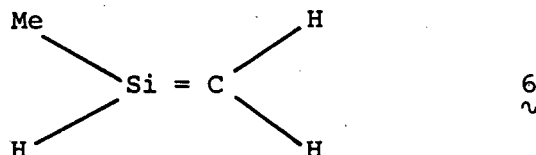
The latter carbene of course is an isomer of the silaethylene  $\underset{\sim}{3}$  and serves as an intermediate between  $\underset{\sim}{1}$  or  $\underset{\sim}{2}$  and  $\underset{\sim}{3}$ .

More recently a considerable amount of additional information concerning the infrared spectra of substituted silaethylenes has appeared. The groups of Gusel'nikov<sup>8</sup> and Nefedov<sup>9</sup> have independently obtained the IR spectra of 1,1-dimethylsilaethylene ( $\underset{\sim}{5}$ )



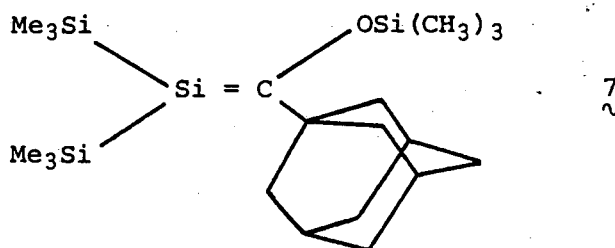
hereafter abbreviated as DMSE. Both groups claim characterization of the Si=C double bond stretching vibration, and their assignments at 1001 cm<sup>-1</sup> and 1003 cm<sup>-1</sup>, are in essential agreement. In a paper to which we will make extensive reference later, Drahnak, Michl, and West<sup>10</sup> (DMW)

have reported the IR spectrum of the monomethylsilathylene (6)



No assignment of the vibrational frequencies was made by DMW, but we may observe that the only frequency near the  $1002\text{ cm}^{-1}$  Russian Si=C assignment is that of DMW at  $986\text{ cm}^{-1}$ .

One of the two most exciting developments in silaolefin chemistry during the past year has been the preparation of the first silaethylene which is stable at room temperature. The importance of this achievement by Brook and coworkers<sup>11</sup> has been greatly enhanced by preliminary single-crystal X-ray studies.<sup>12</sup> In their first communication on the subject Brook, Abdesaken, Gutekunst, Gutekunst, and Kallury<sup>11</sup> reported the synthesis of (7)



along with characterization by IR, NMR, and mass spectrometry. This adamantyl-substituted silaolefin displays a strong IR absorption at  $1135\text{ cm}^{-1}$ , a frequency Brook considers<sup>13</sup> to be a signature of silaethylenes. The crystal structure perhaps surprisingly shows a  $16^\circ$  twist about the C=Si double bond. This slight twisting would on first glance appear to be inconsistent with Chapman's suggestion<sup>5</sup> that the simpler silaethylene 3 has a planar skeletal arrangement and also with theoretical predictions<sup>14,15</sup> that the unsubstituted silaethylene is





not been brought in above since they will be discussed in detail later in conjunction with recent theoretical results. Specifically in this category are the electron diffraction study of DMSE by Mahaffy, Gutowsky, and Montgomery<sup>17</sup> and Conlin and Wood's kinetic study<sup>18</sup> of the isomerization of 6, monomethylsilaethylene. A final recent experimental study of special significance is the observation of the gas phase photo-electron spectrum of dimethylsilaethylene (5) by Koenig and McKenna.<sup>18a</sup>

The experimental studies described above nearly all stand at the frontier of what is presently possible. In every case either the experiment *per se* is difficult or the interpretation is treacherous. Since most silaethylenes (Brook's compound 7 must of course be excluded) are relatively small molecules, it might accordingly be anticipated that some assistance might be rendered from the camp of theoretical chemistry. In fact there is an approaching consensus that molecular electronic structure theory, when carried out with great care using state-of-the-art methods, can be an entirely constructive guide in the interpretation of difficult experiments. This trend has been labelled the "Third Age of Quantum Chemistry" by Richards<sup>19</sup> and provides a general framework for the present Account. Specifically, we will argue that certain critical characteristics of silaolefin chemistry are just beyond the reach of existing laboratory measurements but just within the reach of state-of-the-art theory. Ultimately it seems likely the arbitrator of this healthy rivalry between theory and experiment will be new experiments. Nevertheless we suspect that when the final pages are written, theory will be shown to have played an important role in the silaethylene chapter of chemistry.

### The Length of the Silicon-Carbon Double Bond

As silaethylene chemistry goes, the strength of the Si=C bond is a rather old question. Stated more precisely, the question is "what is the contribution of the  $\pi$  bond to the Si=C dissociation energy?" We have found the recent Account of Walsh<sup>3</sup> to be quite helpful in addressing this issue. Since the Si-C single bond (or  $\sigma$  bond) energy is quite consistently  $\sim 88$  kcal, only a single silaolefin heat of formation is required to fix the  $\pi$ -bond energy.<sup>3</sup> Unfortunately, as Walsh discusses, no such reliable heat of formation exists. Therefore the recommended  $\pi$ -bond energy of  $39 \pm 5$  kcal is based on bond strengths and kinetic arguments.<sup>3</sup> For comparison the analogous carbon-carbon  $\sigma$  and  $\pi$  bond energies are unequivocally known to be  $\sim 85$  kcal and  $\sim 57$  kcal.<sup>20</sup> One concludes that the Si-C and C-C  $\sigma$  bond energies are quite comparable, while present evidence suggests that the Si-C  $\pi$  bond energy is only  $\sim 70\%$  of the C-C  $\pi$  bond energy. Nevertheless, we would conclude (again on the basis of existing evidence) that the  $\pi$ -bond in silaethylenes is a very real bond.

Closely related to the issue of bond strength is that of bond length. Standard single and double carbon-carbon bond lengths are  $1.54 \text{ \AA}$  and  $1.35 \text{ \AA}$ , respectively. If methylsilane  $\text{SiH}_3\text{-CH}_3$  is accepted as the prototype Si-C single bond, then we can take heart in the fact that its Si-C bond distance of  $1.867 \text{ \AA}$  is well established from microwave spectroscopy.<sup>21</sup> If one adopts the admittedly extreme view that the Si=C and Si-C bond distances should lie in the same ratio (0.877) as the C=C to C-C distances cited above

$$\frac{r(\text{Si}=\text{C})_{\text{model}}}{r(\text{Si}-\text{C})} = \frac{r(\text{C}=\text{C})}{r(\text{C}-\text{C})} \quad (3)$$

then the model Si=C bond distance may be empirically predicted to be 1.64 Å. This is probably a lower limit for what might be considered "intuitively reasonable" values of the silicon-carbon double bond distance. If one is a bit more realistic and uses the earlier mentioned bond energy data,<sup>3,20</sup> an empirical formula of the type

$$r(\text{Si}=\text{C})_{\text{realistic}} = r(\text{Si}-\text{C}) + \frac{D_{\pi}(\text{Si}=\text{C})}{D_{\pi}(\text{C}=\text{C})} [r(\text{Si}=\text{C})_{\text{model}} - r(\text{Si}-\text{C})] \quad (4)$$

suggests itself. The application of formula (4) leads to a value of 1.71 Å for  $r(\text{Si}=\text{C})_{\text{realistic}}$ . Although this Si=C bond distance is entirely empirical and based on an assumed relationship between bond distance and bond energy, it does provide a gauge, as it were, by which to think about Si=C internuclear separations.

It may come as a bit of a surprise to the reader that at least nine theoretical predictions of the Si=C double bond distance in the parent silaethylene had been made prior to the experimental determination of the structure of dimethylsilaethylene (5) in the electron diffraction study of Mahaffy, Gutowsky, and Montgomery.<sup>17</sup> These nine theoretical predictions are summarized in Table I. Among the theoretical predictions, the double zeta (DZ) basis set self-consistent-field (SCF) study of Hood and Schaefer<sup>22</sup> is ostensibly the most reliable, followed closely by that of Ahlrichs and Heinzmann,<sup>23</sup> who used a somewhat smaller primitive gaussian basis set. Furthermore, it may be noted that both the Ahlrichs-Heinzmann (1.69 Å) and Hood-Schaefer (1.72 Å) predictions for the Si=C bond distance are in good accord with our empirical

estimate (see previous paragraph) of  $1.71 \text{ \AA}$ .

With the above background in mind, it should become clear to the reader why the present author was quite candidly surprised at the appearance of the electron diffraction report<sup>17</sup> of Mahaffy, Gutowsky, and Montgomery (MGM). Their work of course was pioneering in the sense that it represented the first laboratory determination of any Si=C double bond distance. The MGM experiment was a daring one, as may be seen from the summary of their findings in Table II. Although one does not typically expect from electron diffraction the sort of precision obtainable from microwave spectroscopy, some of the MGM error bars are rather large. Perhaps the most judicious interpretation of the MGM data is that the results of Plate IV, yielding by far the smallest error bars, represent the true electron diffraction structure, while Plates I-III serve primarily to demonstrate in a qualitative way the reproducibility of the experiment.

As noted by MGM,<sup>17</sup> their final experimental value of  $1.83 \pm 0.04 \text{ \AA}$  for the Si=C distance in DMSE lies completely outside the range ( $1.63\text{--}1.75 \text{ \AA}$ ) of the nine earlier theoretical predictions for the parent silaethylene. Since the "best" theoretical<sup>22</sup> Si=C bond distance of  $1.715 \text{ \AA}$  was so much less than the experimental DMSE value of  $1.83 \text{ \AA}$ , one was logically left with three alternatives: (a) the two methyl substituents greatly increase the Si=C distance in DMSE relative to the parent  $\text{H}_2\text{Si}=\text{CH}_2$ ; (b) the theoretical predictions for the Si=C bond distance in  $\text{H}_2\text{Si}=\text{CH}_2$  are all incorrect; (c) the experimental Si=C distance in DMSE is in error. Of course it is also possible that some superposition of these three effects might lead to the  $0.115\text{-\AA}$  gap

between theory for  $\text{H}_2\text{Si}=\text{CH}_2$  and experiment for DMSE. It should be noted that possibility (a) above was fueled by the MINDO/3 prediction of Dewar, Lo, and Ramsden<sup>24</sup> that the Si=C distance in DMSE is  $0.04 \text{ \AA}$  longer than that of the unsubstituted silaethylene.

Faced with the seeming finality of the MGM experiment, we considered it of critical importance to reconsider the structure of silaolefins at a higher level of theory.<sup>25</sup> First, an explicit optimization of the geometrical structure of DMSE itself was carried out. Furthermore, this equilibrium geometry was determined at a level of theory higher than any previous structural optimization of even the parent  $\text{H}_2\text{Si}=\text{CH}_2$ . To the double-zeta (DZ) basis used by Hood and Schaefer<sup>22</sup> was added a set of d functions on each heavy atom. These polarization functions were assigned orbital exponents  $\alpha = 0.75$  (carbon) and  $\alpha = 0.60$  (silicon). The designation of this DZ + d basis set is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), and H(4s/2s).

The predicted theoretical structure for DMSE is seen in Figure 1. The relative orientations of the two methyl groups was arbitrarily chosen to maintain point group  $C_{2v}$ , but the barriers to rotation about these Si-C single bonds should be quite small. Figure 1 shows that the predicted Si=C bond distance,  $1.692 \text{ \AA}$ , falls far outside the range  $1.83 \pm 0.04 \text{ \AA}$  provided by the experimental electron-diffraction study.<sup>17</sup> The predicted Si-C single bond distance,  $1.873 \text{ \AA}$ , is also shorter than experiment,  $1.91 \pm 0.02 \text{ \AA}$ , but in this case the disagreement is much less severe. None of the other geometrical parameters of DMSE were determined by MGM, but the predicted theoretical values are all quite consistent with chemical intuition. In particular, the theoretical

value of  $1.873 \text{ \AA}$  for the Si-C single bond distance in DMSE is only  $0.005 \text{ \AA}$  than that determined by microwave spectroscopy<sup>21</sup> for the prototype  $\text{H}_3\text{Si}-\text{CH}_3$ . Furthermore, a steadily increasing body of comparisons<sup>26,27</sup> between theory and experiment would suggest a typical<sup>28</sup> reliability of  $\pm 0.01 \text{ \AA}$  for bond distances predicted at the DZ + d SCF level of theory.

For an assessment of the relationship between the structures of DMSE and the parent silaethylene, the latter equilibrium geometry was theoretically determined in a manner precisely the same as that described above for DMSE. This DZ + d SCF structure for the parent is illustrated in the middle of Figure 1. Figure 1 shows that at the DZ + d SCF level of theory, the Si=C bond distances of  $\text{H}_2\text{Si}=\text{CH}_2$  and  $(\text{CH}_3)_2\text{Si}=\text{CH}_2$  are identical ( $1.692 \text{ \AA}$ ) to within one-thousandth of an angstrom. This would appear to make rather unlikely the possibility, suggested by MINDO/3 calculations<sup>24</sup> and cited by MGM, that the Si=C distance is significantly longer in DMSE.

The only remaining satisfactory explanation of the experimental DMSE geometry is that the DZ + d SCF level of theory systematically predicts Si=C distances much too short. This possibility has been examined by explicitly determining the structure of  $\text{H}_2\text{Si}=\text{CH}_2$  using highly correlated<sup>29</sup> wave functions. Using the DZ + d basis set, configuration interaction (CI) was carried out including all single and double excitations relative to the Hartree-Fock reference configuration. With the six core orbitals  $[\text{C}(1s), \text{Si}(1s, 2s, 2p_x, 2p_y, 2p_z)]$  constrained to be doubly occupied in all configurations, this approach yields a total 6920  $^1\text{A}_1$  configurations.

The DZ + d CI structure of silaethylene shown at the bottom of Figure 1 demonstrates clearly that electron correlation has little effect on the predicted Si=C bond distance. The theoretical distance is  $1.705 \text{ \AA}$ , or only  $0.013 \text{ \AA}$  longer than the analogous SCF result. From the above-discussed comparison of the silaethylene and DMSE structures, one anticipates that the DMSE Si=C bond distance will also be  $\sim 1.71 \text{ \AA}$ . This conclusion is supported by the subsequent work of Hanamura, Nagase, and Morokuma,<sup>30</sup> who used a generalized valence bond approach in concert with a smaller basis set to predict a Si=C distance of  $1.728 \text{ \AA}$ .

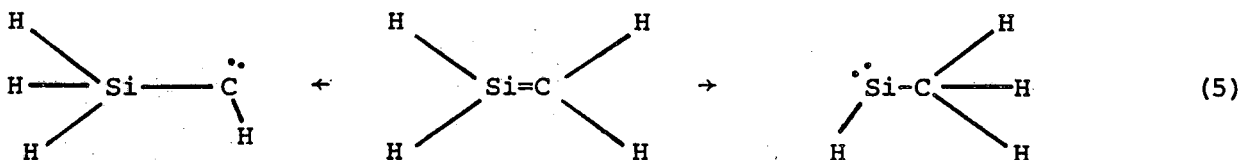
On the basis of previous experience,<sup>26,27</sup> we suggest that the exact (unknown) Si=C bond distance  $r_e$  for the unsubstituted silaethylene is  $1.705 \pm 0.03 \text{ \AA}$ . To our thinking this prediction casts serious doubt upon the assumptions made by MGM in extracting the Si=C distance in DMSE from the reported electron-diffraction data.<sup>17</sup>

Before concluding this section, some discussion of the recent crystal structure of the adamantyl- and trimethylsilyl-substituted compound **7** is mandatory. As noted earlier this molecule is twisted by about  $16^\circ$  about the Si=C double bond and has a silicon-carbon internuclear separation of  $1.764 \text{ \AA}$ . We concur with Brook<sup>4</sup> that this twisting may be due to the bulky substituents and not a property of the parent silaethylene. Perhaps more important, it must be noted that twisting about the Si=C bond destroys the  $\pi$  bond when the twisting angle becomes  $90^\circ$ . For a twist angle of  $90^\circ$ , one is left with a single-bonded diradical, with an Si-C bond distance expected to be comparable to the  $1.88 \text{ \AA}$  predicted for triplet silaethylene.<sup>22</sup> For this reason, we do not consider Brook's silicon-carbon bond distance<sup>12</sup> of  $1.764 \text{ \AA}$

for the silaolefin  $\tilde{7}$  to be in conflict with the theoretical results presented above.

#### The Barrier Separating Silaethylene from Methylsilylene

Since the weakest bond dissociation energy in silaethylene exceeds 80 kcal,<sup>3</sup> the only possible low-energy pathways in the absence of collisions are intramolecular rearrangements. Specifically, the 1,2 hydrogen shift<sup>31</sup> connects silaethylene with both methylsilylene and silylmethylene:



The rearrangement of silaethylene to methylsilylene is of particular importance, since (as will be discussed in detail in the next section) these two isomers are nearly degenerate.<sup>32</sup> Given that the right half of reaction (5) is nearly thermoneutral and that one of these two singlet species is the absolute minimum on the  $\text{SiCH}_4$  potential energy hypersurface, the barrier height between silaethylene and methylsilylene becomes an important issue.

The first theoretical study of the barrier between the singlet electronic ground states of  $\text{H}_2\text{Si}=\text{CH}_2$  and  $\text{H}\ddot{\text{Si}}-\text{CH}_3$  was that of Goddard, Yoshioka, and the present author (GYS).<sup>33</sup> The stationary point geometry expected to correspond to the transition state was determined at the double zeta basis set, self-consistent-field (DZ SCF) level of theory. Subsequently all quadratic force constants were determined and this

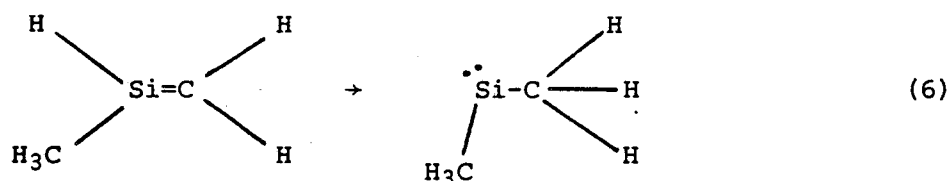


stationary point was proven to be a transition state via a harmonic vibrational analysis, which showed a single imaginary frequency ( $1167i \text{ cm}^{-1}$ ). The transition state was predicted to lie 45.0 kcal above the reactant silaethylene. Given this DZ SCF transition state geometry and the analogous structure for silaethylene, the barrier height was predicted at three additional levels of theory. Configuration interaction including all (core orbitals Si 1s2s2p, C 1s deleted) single and double excitations (CISD) amounted to 10,585 configurations for the transition state and yielded a barrier of 43.4 kcal. When the Davidson correction<sup>34</sup> for the effect of higher excitations (unlinked clusters) was appended to reactant and transition state, the barrier was reduced to 41.0 kcal. Finally, the effect of d functions on silicon and carbon was tested at the SCF level only and had little effect, reducing the barrier from 45.0 (DZ SCF) to 44.6 (DZ + d SCF).

The level of theory applied by GYS to the silaethylene rearrangement barrier was reasonable, but not state-of-the-art. This is understandable if one appreciates that this barrier was just one of a large number of issues considered by GYS relating the singlet and triplet electronic states of silylmethylene, silaethylene, and methylsilylene.<sup>33</sup> The subsequent examination of analogous studies (of hydrocarbons, such as the vinylidene  $\rightarrow$  acetylene rearrangement)<sup>35</sup> would appear to suggest that extension of the basis set, treatment of higher order correlation effects, and correction for zero-point vibrational energies would all reduce the predicted barrier, but not to less than 25 kcal.

In light of this theoretical background, the publication of dissenting back-to-back experimental communications<sup>10,18</sup> in the Journal

of the American Chemical Society left us temporarily at a loss for words. The fact that one of these experimentalists is a personal friend provided little in the way of consolation. Conlin and Wood<sup>18</sup> reported kinetic evidence that the reaction of methylsilylaethylene to dimethylsilylene



is rapid. Specifically they point to the pyrolysis of methylsilacyclobutane leading to the isolation of products characteristic of dimethylsilylene reactions. Moreover, Conlin and Wood suggested that the isomerization (5) of the parent silaethylene might be even more rapid than (6).

In the second communication, Drahnak, Michl, and West (DMW)<sup>10</sup> present matrix isolation results which suggest that reaction (6) proceeds rapidly at 100° K, and the product dimethylsilylene is then trapped. DMW cite the previously discussed GYS theoretical study<sup>33</sup> but conclude that "unless the additional methyl [i.e., the difference between reactions (5) and (6)] has a dramatic effect, this (theoretical) result is not compatible with our interpretation. No simple alternatives have occurred to us." Thus there appeared to be a conflict between the theoretical expectation<sup>33</sup> that the barrier is not less than ~25 kcal and the experimental deduction that this same barrier is perhaps 5 kcal or less.

As with the conflict involving the structure of dimethylsilaethylene, this apparent discrepancy between theory and experiment made it

imperative to re-examine the barrier height for (5) at a higher level of theory.<sup>36</sup> Specifically, it was thought that the addition of polarization basis functions might significantly alter the earlier predictions.<sup>33</sup> Therefore a set of p functions (orbital exponent  $\alpha = 1.0$ ) was added to each of the four hydrogen atoms, as were d functions on carbon and silicon. The technical specification of this double zeta plus polarization (DZ + P) basis set is then Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), H(4s1p/2s1p). Although heavy atom d functions are known<sup>37</sup> to sometimes be important for such systems, it was also thought that the p functions on hydrogen (particularly the migrating hydrogen) might lower the predicted barrier.

The transition state geometry for the silaethylene rearrangement was accordingly redetermined at the DZ + P SCF level of theory and is illustrated here in Figure 2 along with the analogous structure for silaethylene. Note that the small differences between the  $\text{H}_2\text{Si}=\text{CH}_2$  structures in Figures 1 and 2 are due to the addition of hydrogen p functions in the latter case, i.e. the structure in Figure 1 was determined with a DZ + d basis, while that of Figure 2 was obtained using the fully polarized DZ + P basis. Comparison of the DZ + P SCF transition state structure of Figure 2 with the earlier DZ SCF result of GYS<sup>33</sup> shows the two stationary points to be qualitatively similar. Moreover the DZ + P SCF barrier height for reaction (5) is 44.7 kcal, only 0.3 kcal below the DZ SCF barrier. Thus it is seen that at the SCF level the addition of polarization functions has little effect on either the reaction mechanism or energetics.<sup>36</sup>

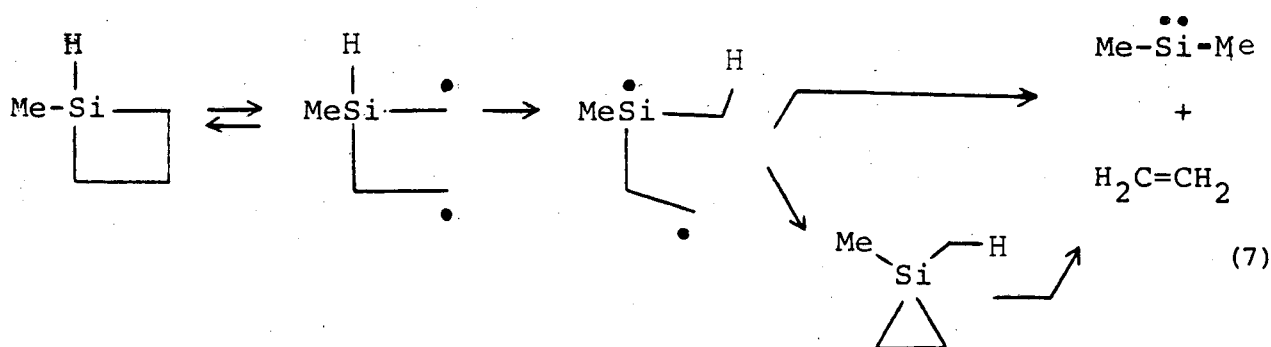
With the full DZ + P basis set and assuming the SCF geometrical structures of Figure 2, CI including all single and double excitations

was carried out with the restriction that the core molecular orbitals were deleted. For the transition state, containing no elements of point group symmetry other than the identity (point group  $C_1$ ), the CI involved 32,131 configurations. The variational energies thus obtained for silaethylene and the rearrangement transition state were -329.29703 and -329.22858 hartrees, respectively, yielding a barrier of 43.0 kcal. Appendage of the Davidson correction<sup>34</sup> for higher excitations yields a final prediction of 40.6 kcal for the classical barrier.

Even if further refinement of the wavefunctions lowered the barrier an additional 10 kcal (we consider this unlikely) and zero-point vibrational energy corrections make the activation energy 5 kcal less than the classical barrier,<sup>38</sup> one is still left with a theoretical activation energy of 25 kcal. In our opinion, the body of theoretical evidence supporting a high (>25 kcal) barrier for the silaethylene rearrangement (5) has thus become sufficiently weighty that alternate interpretations of the Conlin and Wood<sup>18</sup> and Drahnak, Michl, and West<sup>10</sup> experiments should be sought.

A substantive effort toward the reinterpretation of the Conlin and Wood experiment<sup>18</sup> has recently been made, and being of direct relevance to the topic at hand, some discussion is in order here. Specifically Barton, Burns, and Burns<sup>39</sup> introduce a note of caution in the interpretation of silaethylene rearrangement results from silacyclobutane pyrolyses. Barton points to a body of data suggesting that silacyclobutanes may undergo thermal decomposition initially through C-C rather than Si-C ring-bond homolysis.<sup>40</sup> Should this be the

case, than the 1,2 shift might occur at the diradical stage [rather than via reaction (6)], from which Barton has proposed two pathways<sup>39</sup>



to dimethylsilylene, and neither of these involves methylsilaethylene. A series of experiments to test this mechanism was designed by Barton<sup>39</sup> and appears to significantly weaken the Conlin-Wood interpretation that methylsilylaethylene is formed by the pyrolysis of methylsilacyclobutane.

Only one conceivable reinterpretation of the DMW matrix isolation results<sup>10</sup> has occurred to us, other than the obvious possibility (probably just wishful thinking) that the molecule they assign as methylsilaethylene (6) is something else. Our thought here is that although methylsilaethylene may be formed in the DMW experiment, it rapidly dimerizes to the disilacyclobutane, which could conceivably go on to produce dimethylsilylene by some (perhaps bimolecular) mechanism not involving reaction (6). In any case, further experiments would very much appear in order in the face of such compelling theoretical evidence<sup>33,36</sup> that the barrier for the parent silaethylene rearrangement is substantial.

### The Energy Difference Between Silaethylene and Methylsilylene

The activation energy for rearrangement of silaethylene to methylsilylene is clearly related to the energy separation between these two potential minima. If Drahnak, Michl, and West's interpretation of their experiment<sup>10</sup> is correct and this rearrangement (5, right hand side) occurs unimolecularly at 100° K, then methylsilylene necessarily lies energetically below silaethylene. The same conclusion follows from the work of Conlin and Wood,<sup>18</sup> but other experiments suggest a different conclusion. For example Auner and Grobe<sup>41</sup> claim to have prepared silaethylene from the pyrolysis of either silacyclobutane or 1,3-disilacyclobutane, and that  $\text{H}_2\text{Si}=\text{CH}_2$  can be stored in the condensed phase at 77° K for several months.

Although Maier, Mihm, and Reisenauer<sup>16</sup> state specifically that their results contradict the findings of Auner and Grobe, in a second paper<sup>42</sup> they present interesting evidence against the notion that methylsilylene lies lower than silaethylene and that the two are separated by only a small barrier. In this significant paper by Rosmus, Bock, Solouki, Maier, and Mihm<sup>42</sup> are presented reliable theoretical predictions of the photoelectron spectrum (PES) of the parent silaethylene, followed by a report of the experimental PES. Of great importance in the present context is the statement by Rosmus, *et. al.*<sup>42</sup> that the pronounced vibrational fine structure of the first PE band resembles that of the iso(valence)electronic ethylene. More specifically they state that "the vibrational progressions assigned preclude, with a high degree of probability, the presence of isomers such as  $\text{CH}_3\text{SiH}$  or  $\text{H}_3\text{SiCH}$ ." Since this PES was recorded at 850° K,

it would appear logical to conclude that either (a) methylsilylene lies higher in energy than silaethylene or (b) there is a significant barrier separating the two (as predicted by theory<sup>33,36</sup>). Of course Maier's PES<sup>42</sup> also allows for the possibility that both (a) and (b) above are true. In any case, it seems difficult to avoid the inference that this experiment is suggesting exactly the opposite conclusion to that drawn by Coulin and Wood<sup>18</sup> and by DMW.<sup>10</sup>

It is almost invariably instructive to examine in hindsight the results of theoretical predictions made prior to the existence of experimental answers. Under such circumstances the theory is forced to be "honest", i.e. the temptation to adjust the theory to fit the known answer is not present. In this context, Table III enumerates eight predictions of the energy difference between the singlet ground states of silaethylene and methylsilylene, all made prior to the Conlin and Wood<sup>18</sup> and DMW<sup>10</sup> experimental reports. The predictions of Gordon<sup>32</sup> were particularly timely, being the first of their kind and apparently the first suggestion from any source that methylsilylene might actually be the absolute minimum on the  $\text{SiCH}_4$  potential energy hypersurface. Although the present author had a prior interest<sup>22</sup> in silaethylene molecular structures and the singlet-triplet separation, the intriguing prediction of Gordon<sup>32</sup> concerning the stability of methylsilylene led us to a much more detailed theoretical study of the  $\text{SiCH}_4$  energy surface.

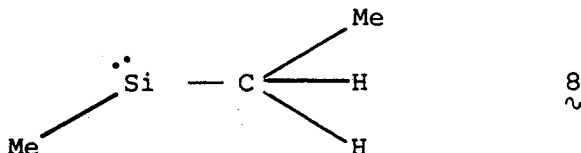
Gordon's most reliable level of theory suggests that methylsilylene lie  $\sim 7$  kcal below silaethylene. The subsequent, more complete theoretical study of GYS<sup>33</sup> brings the two isomers much closer energetically, with the final prediction that methylsilylene lies

only 0.4 kcal below silaethylene. GYS suggest "an estimated uncertainly in (this) energy difference of 5 kcal" and hence the theoretical conclusion that the two isomers are essentially degenerate. Subsequently, comparable (with the exception that a pseudopotential was employed by Trinquier and Malrieu) theoretical studies<sup>43</sup> have come to a similar conclusion. Thus the two most reliable theoretical perspectives<sup>33,43</sup> do not support the experimental conclusion<sup>10,18</sup> that methylsilylene lies energetically below silaethylene by a significant amount.

In the preliminary stages of the preparation of this Account, it was decided to make a more definitive prediction of the above discussed energy difference. In this vein, Bicerano<sup>44</sup> carried out a complete optimization of the structure of methylsilylene at the fully polarized DZ + P SCF level of theory. This theoretical structure is included at the bottom of Figure 2. The energy of methylsilylene obtained in this way is 3.7 kcal below the analogous energy of silaethylene. When DZ + P CI is carried out in a manner comparable to that described previously<sup>36</sup> for silaethylene, 16,941 configurations are included variationally and the total energy obtained is -329.29625 hartrees. These correlated wave functions allow us to predict that methylsilylene lies 0.5 kcal above silaethylene. Appendage of the Davidson correction<sup>34</sup> for higher excitations yields the final prediction that methylsilylene lies 1.7 kcal above silaethylene.



A closely related and important theoretical study which requires some discussion here is that of Hanamura, Nagase, and Morokuma.<sup>30</sup> These authors predicted the energy difference between dimethylsilaethylene (5) and its 1,2 methyl shifted isomer



at several levels of theory. As illustrated in Table III for the parent, improving the level of theory consistently lowers the silaolefin relative to the silylene. Morokuma's final prediction is that dimethylsilaethylene lies 22 kcal below  $\tilde{8}$ . If this is indeed true, it means that the two methyl substituents significantly lower the energy of the silaolefin relative to its silylene isomer. Morokuma<sup>30</sup> has also predicted the vibrational frequencies of DMSE and finds an intense Si=C stretching band near  $1000 \text{ cm}^{-1}$ , in agreement with the experimental assignments of Gusel'nikov<sup>8</sup> and Nefedov.<sup>9</sup> However, Morokuma sounds a note of caution in mentioning that the silylene isomer  $\tilde{8}$  also has a moderately strong  $\text{CH}_3$  rocking mode near  $1000 \text{ cm}^{-1}$ .

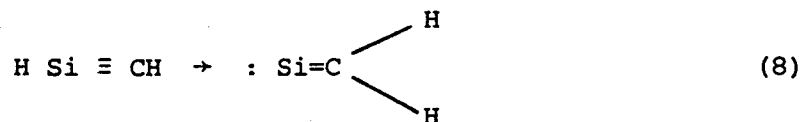
#### Concluding Remarks

This account has concentrated on three questions for which there appear (at present) to be striking conflicts between theory and experiment. Although we suspect that theory is correct in all three cases, these apparent discrepancies will in all probability be ultimately adjudicated by new and definitive experiments. We await such new

experiments with much interest.

There are a number of reliable and interesting silaolefin predictions from theory for which there are as yet no directly pertinent experiments. For example, the geometrical structure of triplet silaethylene has been predicted<sup>22,23,45</sup> to be both twisted (about the Si-C bond) and pyramidalized (with respect to the silicon atom). Moreover, triplet silaethylene has been predicted to lie only ~40 kcal above the singlet electronic ground state.<sup>22</sup> It will be important to see whether these predictions hold up under experimental scrutiny.

A more general question for the future is that if silaolefins can now be observed in the laboratory almost routinely, what about silaacetylenes? For the parent molecule, Murrell, Kroto, and Guest<sup>46</sup> established theoretically some time ago that the isomerization



is substantially exothermic. That is, the silylidene :Si=CH<sub>2</sub> is the absolute minimum on its potential energy hypersurface. Moreover, Hopkinson and Lien<sup>47</sup> subsequently discovered that the linear HSiCH is not even a minimum on the potential surface. However, all is not lost in light of Gordon and Pople's finding<sup>48</sup> that silaacetylene favours a bent equilibrium geometry. The only (as best we can determine) predicted equilibrium geometry for silacetylene is that of Hoffmann,<sup>49</sup> seen in Figure 3, which reveals a *trans* bent structure. The silicon-carbon bond distance (1.64 Å) is significantly less than in silaethylene

(1.71 Å), but notably longer than would be anticipated for a hypothetical Si≡C triple bond. A *cis* bent equilibrium geometry also appears possible, and work in progress is designed to pursue this and other points.<sup>49</sup> It may also be hoped that a suitable choice of substituents might actually place the silaacetylene energetically below the silylidene isomer. Experiments probing the latter point would be particularly welcome.

#### Acknowledgments

Particular thanks are due to Dr John D. Goddard for many stimulating and informative discussions and for his contributions to the research reviewed here. I am also grateful to Diane Hood, Yasunori Yoshioka, Jozef Bicerano, and Mark Hoffmann, who carried out much of the work described in this Account. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098, the National Science Foundation under Grant Number CHE-8009320, the Robert A. Welch Foundation, and the University of Texas. The hospitality and intellectual stimulation provided by Professor David P. Craig and Dr. Leo Radom at the Australian National University, where this Account was composed, are sincerely appreciated.

#### Figure Captions

Figure 1. Theoretical equilibrium geometries for 1,1-dimethylsilaethylene (DMSE) and the parent unsubstituted silaethylene. All bond distances are in Å.

Figure 2. Theoretical structures for silaethylene, methylsilylene, and the transition state connecting them.

Figure 3. Theoretical equilibrium geometry for *trans* silaacetylene predicted at the DZ + P CI level of theory.

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Table I. Theoretical values of the Si=C bond distance (in Å) in silaethylene, predicted before the electron diffraction experiment of Mahaffy, Gutowsky, and Montgomery.<sup>17</sup>

r(Si=C)	Year	Method	Authors
1.75	1974	CNDO/2	R. Damrauer and D.R. Williams, J. Organomet. Chem. <u>66</u> , 241 (1974)
1.630	1975	MINDO/3	Dewar, Lo, and Ramsden, Reference 24.
1.693	1975	4-31G SCF	Schlegel, Wolfe, and Mislow, Reference 14.
1.638	1976	FSGO SCF	P.H. Blustin, J. Organomet. Chem. <u>105</u> , 161 (1976).
1.666			
1.637	1976	STO-4G SCF	O.P. Strausz, L. Gammie, G. Theodorakoupoulos, P.G. Mezey, and I.G. Csizmadia, J. Amer. Chem. Soc. <u>98</u> , 1622 (1976).
1.69	1977	DZ SCF	Ahlrichs and Heinzmann, Reference 23.
1.715	1978	DZ SCF	Hood and Schaefer, Reference 22.
1.637	1978	STO-3G SCF	H.B. Schlegel, B. Coleman and M. Jones, J. Amer. Chem. Soc. <u>100</u> , 649 (1978).
1.71	1979	Pseudopotential SCF	J.-C. Barthelat, G. Trinquier, and G. Bertrand, J. Amer. Chem. Soc. <u>101</u> , 3785 (1979).



Table II. Structural results of the electron diffraction experiments of Montgomery<sup>17</sup> on molecule 5, dimethylsilaethylene.

	$r(\text{Si}=\text{C}), \text{\AA}$	$r(\text{Si}-\text{C}), \text{\AA}$
Plate I	$1.832 \pm 0.064$	$1.903 \pm 0.035$
Plate II	$1.815 \pm 0.036$	$1.908 \pm 0.017$
Plate III	$1.835 \pm 0.041$	$1.906 \pm 0.020$
Plate IV	$1.832 \pm 0.005$	$1.905 \pm 0.003$

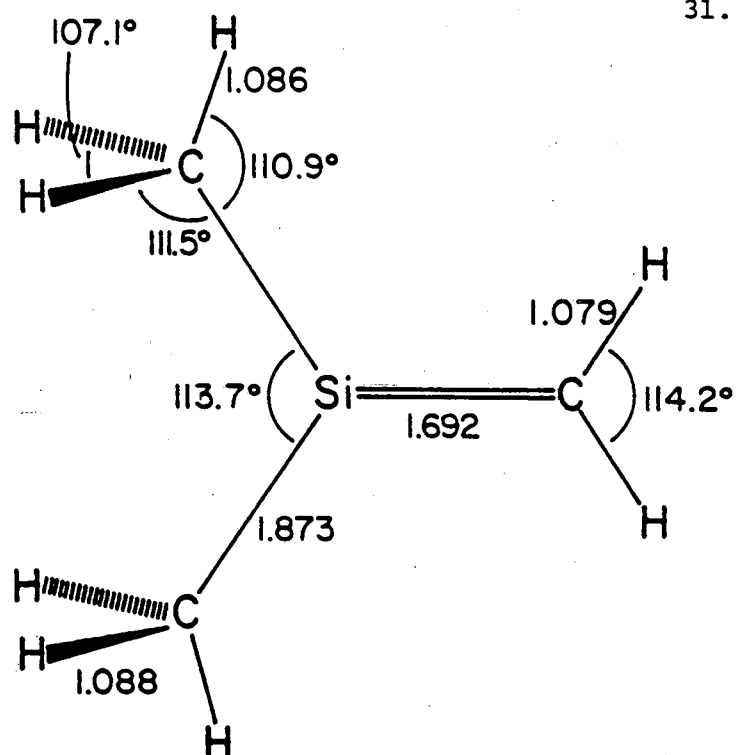
Table III. Theoretical predictions of the energy difference (in kcal) between silaethylene and methylsilylene made prior to the experiments of Conlin and Wood<sup>18</sup> and Drahnak, Michl, and West.<sup>10</sup>

$\Delta E(\text{H}_2\text{Si}=\text{CH}_2 \rightarrow \text{HSiCH}_3)$	Year	Method	Authors
-23.2	1978	STO-4G SCF	Gordon, Reference 32
-9.2		STO-3G+d SCF	
-12.5		STO-4G CI	
-6.8		STO-3G+d CI	
-11.6	1980	DZ SCF	Goddard, Yoshioka, and
			Schaefer, Reference 33
-2.3		DZ CI	
-4.9		DZ+d SCF	
-0.4		DZ+d CI	

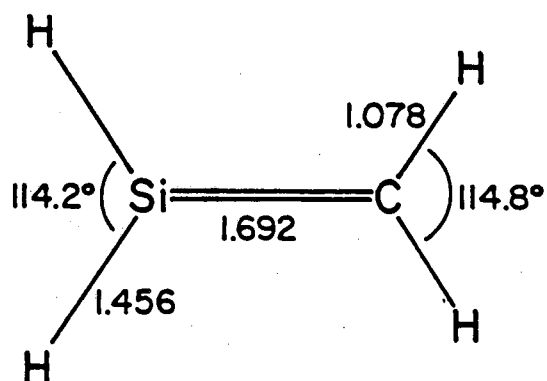
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DZ+d SCF



DZ+d SCF



DZ+d CI

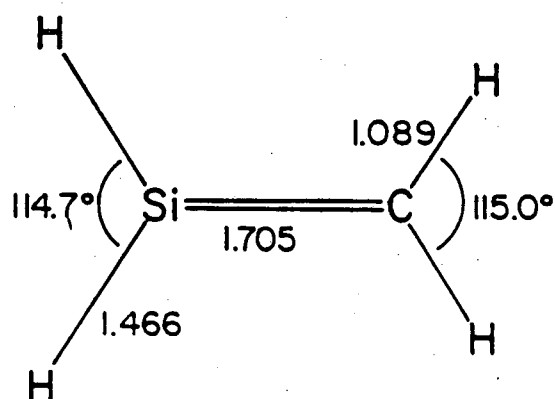


Figure 1

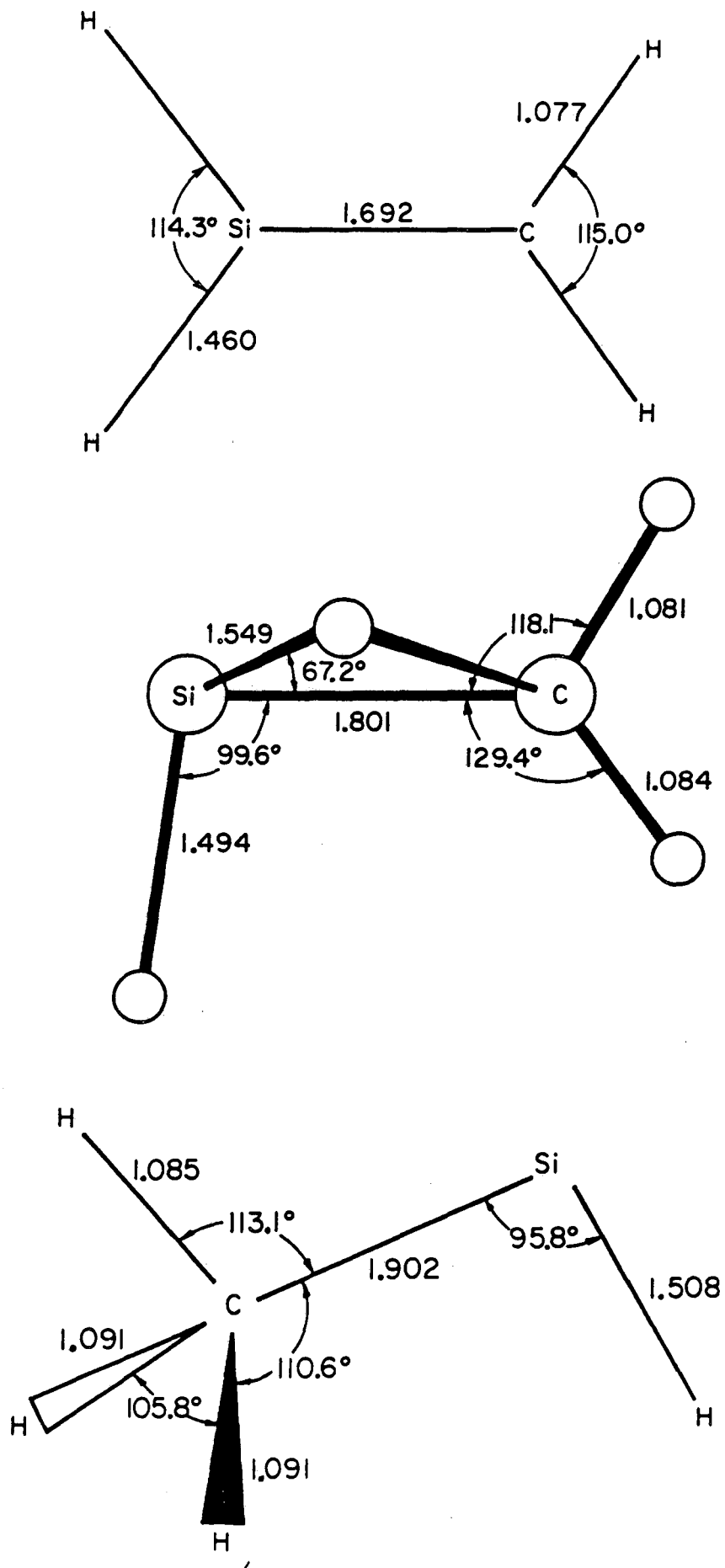


Figure 2

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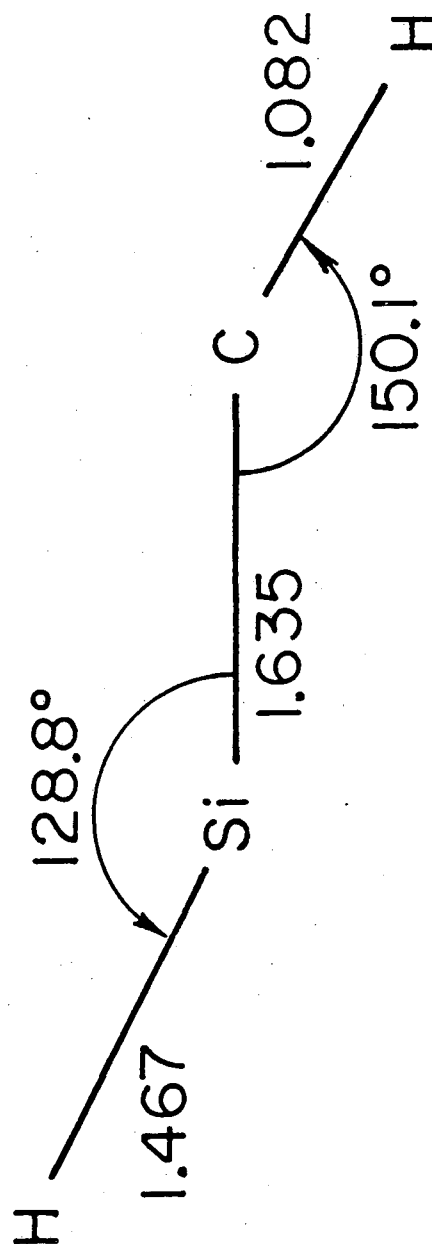


Figure 3

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