semiconducting phases display ranges of oxygen solubility.[5,6]

Figure 1 shows the Raman spectra of both the $YBa_2Cu_3O_7$ and the $YBa_2Cu_3O_6$ phases in the Cu–O stretching region. These materials are very weak Raman scatterers, due primarily to the small volume sampled in such highly absorbing solids. Consequently, we found it necessary to use a very sensitive multichannel Raman spectrometer (described in detail elsewhere[12]) to acquire these data at the very low laser power (10~20 mW) necessary to avoid sample damage. The laser beam impinged on the sample disk at an angle of incidence of 75° to the surface normal with the scattered radiation collected along the normal. No significant polarization effects were found, which is consistent with the polycrystalline nature of the samples.

The striking feature of the spectra is the near invariance of two of the mode frequencies to composition, while there is a dramatic shift of the third to lower frequency in the oxygen deficient compound. The unit cell of the O_6 compound has D_{4h} symmetry, while the O_7 unit cell symmetry is D_{2h}. Of the ten Raman active modes in each compound, there are only four that involve Cu–O stretching motions; normal coordinate analysis identifies three associated with the CuO_2 sheets and one with the CuO_3 chains. We therefore assign the modes at 502 and 589 cm^{-1} to the symmetric and asymmetric stretches of the square pyramidal CuO_2 layers parallel to the *ab* plane (refer to Figure 1 in ref 5), since they are common to both structures. The asymmetric stretch is a degenerate pair in the O_6 compound but should be split in the O_7 compound; that we don't resolve the splitting reflects the small departure from D_{4h} symmetry and the relatively large line widths involved. We note, but do not assign, the appearance of a broad shoulder near 591 cm^{-1} in the O_6 material. The intense Raman band occurring at 636 cm^{-1} in the O_7 material is due to the corner sharing coplanar CuO_3 chains parallel to the *b*-axis in the *bc* plane. In contrast to the CuO_2 layer structural unit, there are two inequivalent types of Cu–O bonds in the CuO_3 chain structural unit, i.e., the terminal Cu–O bonds along the *c*-axis and the bridging Cu–O bonds along the *b*-axis. Only the symmetric mode involving the terminal Cu–O stretching motions is Raman active. The intensity of this mode is preserved in the O_6 material, but its frequency is shifted to 344 cm^{-1}. This large frequency shift is easily explained by considering the bonding in the two compounds. As the bridging oxygens are lost in the O_6 material the formal oxidation state on the copper is reduced from Cu^{III} to Cu^{I}, taking on a d^{10} configuration. In considering a filled d-shell, the bonding is expected to involve sp σ bonds which should be much weaker than the bonding in the O_7 material (which involves the $d_{x^2-y^2}$ orbital). The reduced bond strength manifests itself in the lower vibrational frequency. The only difficulty with this interpretation is that the crystal structure data show very similar terminal Cu–O bond lengths (~1.85 Å) in both compounds.[5,13]

In conclusion, we have identified a high-frequency mode in the Raman spectrum of the high temperature superconductor $YBa_2Cu_3O_7$ which is shifted to much lower frequencies in the oxygen deficient nonsuperconducting compound $YBa_2Cu_3O_6$. This mode is assigned to the symmetric stretch of the terminal Cu–O bonds in the linear chain of corner-shared CuO_3 units; this assignment is consistent with the structural models derived from diffraction experiments. While these experiments do not definitively establish a causal link between the frequency shift of this mode and superconductivity, the correlation is nevertheless intriguing. Polarization experiments using single crystals of these materials as well as determination of the behavior of the spectrum as the temperature is lowered through T_c are clearly required to firm up the spectral assignments and determine the relevance of the phonons to the superconducting behavior. Such experiments are underway in our laboratory.

Acknowledgment. We gratefully acknowledge the financial support of the Materials Research Group by the National Science Foundation under Grant DMR-8418086.

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(13) Cox, D. E.; Moodenbaugh, A. R.; Hurst, J. J.; Jones, R. H. *J. Phys. Chem. Solids* **1987**, in press.

Silathione ($Me_2Si{=}S$) Extrusion in the Thermolysis of Silylthioketenes

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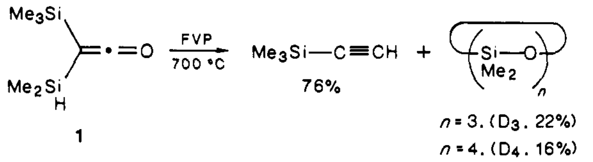
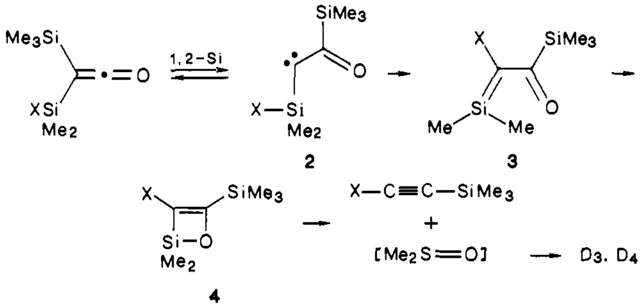
Recently we reported that certain silylketenes underwent a remarkable thermal extrusion of dimethylsilanone, $Me_2Si{=}O$.[1] Thus, for example, ketene **1** undergoes flash vacuum pyrolysis (FVP) at 700 °C to cleanly afford trimethylsilylacetylene and a mixture of permethylcyclosiloxanes, presumably derived from oligomerization of dimethylsilanone.

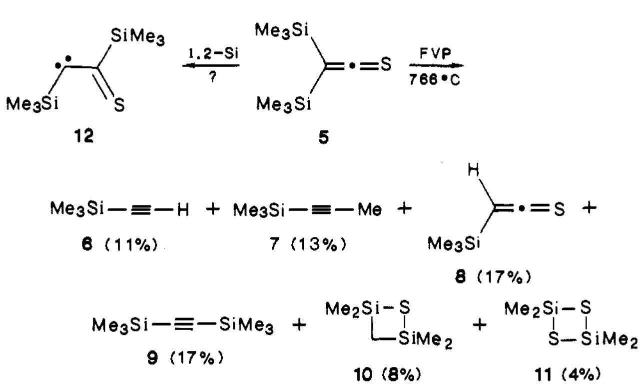


Of considerable interest is the possibility that the decompositions of silylketenes proceed through a "retro-Wolff" rearrangement. Such a process would be initiated by a 1,2-silyl shift to produce an α-ketocarbene **2** which could proceed to products by isomerization to silene **3**,[2] closure to silaoxetene **4**, and a formal retro "2 + 2" to silanone and acetylene.



It was of obvious interest to see if the decomposition route for silylketenes could be extended to other heterocumulenic systems. To this end we have examined, and preliminarily report here, the thermolysis of silylthioketenes.

FVP of bis(trimethylsilyl)thioketene[3] (**5**) at 768 °C resulted in 47% conversion and the formation of the seemingly complex mixture of products **6**–**11** for which the yields have been corrected for unreacted **5**.[4]



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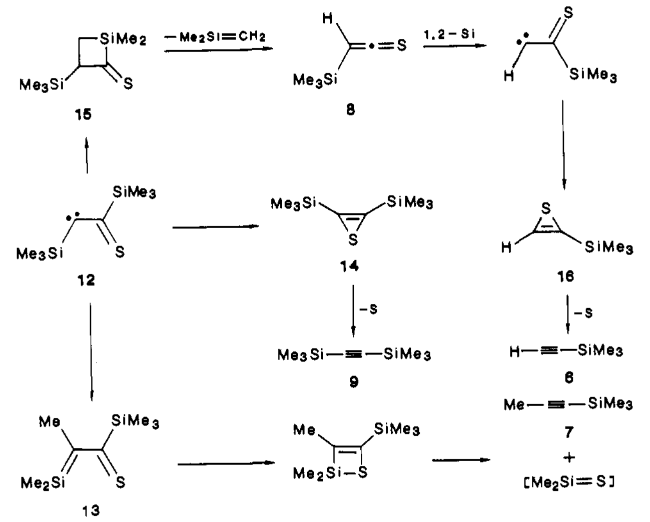
(1) Barton, T. J.; Groh, B. L. *J. Am. Chem. Soc.* **1985**, *107*, 7221.

(2) In our preliminary report,[1] it was thought that it might be necessary to have an Si–H for this rearrangement. We now know that this is not a requirement and will soon report a more inclusive study of silylketene decomposition as well as complete details of our work in silylthioketene thermolysis.

(3) Harris, S. J.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1008.

0002-7863/87/1509-5292$01.50/0

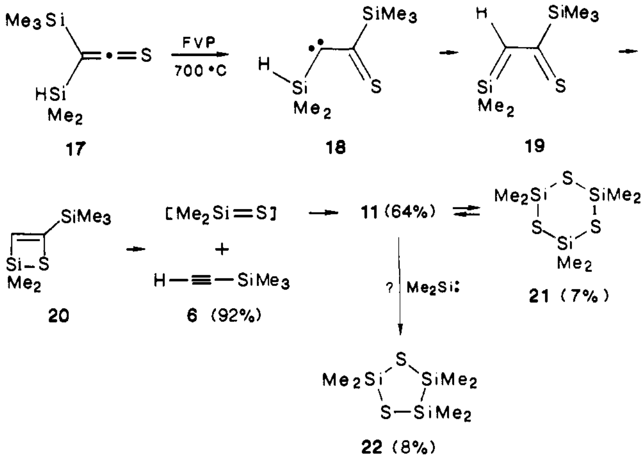
Scheme I



The complexity of the product mixture from **5** is considerably reduced when it is recognized that every one of the products **6–11** can be mechanistically rationalized by processes each initiated by isomerization of **5** to α-thioketocarbene **12** via a 1,2-shift of Me_3Si. Our proposals for the routes to **6–11** all originating from carbene **12** are incorporated into Scheme I. Rearrangement of **12** by 1,2-methyl migration from silicon produces silene **13** which would, in analogy to the mechanism proposed for silylketenes, be expected to close and decompose to acetylene **7** and dimethylsilathione ($Me_2Si{=}S$). Isomerization of **12** to thiirene **14** affords a path to acetylene **9** by extrusion of atomic sulfur. Although we are aware of no precedent for this latter process, MNDO calculations by McKee[5] have directly linked $S(^1D)$ and acetylene to thiirene. Formation of thioketene **8** is explained by intramolecular C–H insertion by carbene **12** to produce silacyclobutane **15** followed by silene extrusion. Thioketene **8** would be expected, by analogy to the **12** → **9** transformation, to isomerize to thiirene **16** and extrude sulfur to afford product **6**. Cyclic products **10** and **11** correspond to reaction of $Me_2Si{=}Si$ with either $Me_2Si{=}CH_2$ or another molecule of silathione. Thus, all products are readily rationalized as arising from a single initial intermediate, carbene **12**.

The apparent complexity of the product mixture arising from thermolysis of **5** is drastically reduced by the simple modification of replacing one methyl group by hydrogen. Thus, FVP of (dimethylsilyl)(trimethylsilyl)thioketene (**17**)[6] at 700 °C (Scheme II) results in 100% conversion of **17** and formation of (trimethylsilyl)acetylene (**6**) in a remarkable 92% yield accompanied by cyclosilathianes **11** and **21** in a combined yield of 71%. Both **11** and **21** are thought to be products of the cyclic oligomerization of dimethylsilathione, $Me_2Si{=}S$,[7] and are known to thermally equilibrate.[8] Thus, once again all major products are easily rationalized as originating from an initial 1,2-silyl migration on the heterocumulenic π-framework.[9] We can only speculate that product **22** arises from Me_2Si: (perhaps from reductive elimination in **17**?) insertion into **11** as has been suggested by Weber.[10]

Scheme II



Both the lower thermal requirements and the higher yield of silathione extrusion products for **17** as opposed to **5** are paralleled in the thermochemistry of the analogous silylketenes[2] and may be explained by the greater migratory aptitude of hydrogen (**18** → **19**, Scheme II) as compared with methyl (**12** → **13**, Scheme I).

Our eventual complete manuscript on the thermochemistry of both silylketenes and silylthioketens will also describe current studies on silathione trapping and kinetic studies on these decompositions.

Acknowledgment. We gratefully acknowledge the National Science Foundation for support of this work.

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[4] All previously reported products were identified by PMR, CMR, exact mass, and comparison with literature values. Because of instability and separation difficulties, **8** was only characterized by the following: PMR δ 3.52 (s 1 H), 0.204 (s, 9 H); CMR δ (−0.032, 49.94, 220.87); MS, relative intensity 130 (M^+, 18), 115 (79), 73 (97), 57 (32), 53 (38), 43 (100), 39 (36), 32 (36); IR (C=C=S, 1744 cm^{-1}). Yields are calculated from calibrated GC measurements.

[5] McKee, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 5059.

[6] Synthesized by a method analogous to that in ref 3. Thioketene **17** was characterized by the following: PMR δ 4.24 (sept, 1 H), 0.31 (d, 6 H), 0.23 (s, 9 H); CMR δ (−2.34, 0.17, 49.49, 213.66); exact mass calcd 188.05113, measured 188.05118, and satisfactory elemental analysis for C, H, and S.

[7] Gusel'nikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.

[8] Moedritzer, K. *J. Organomet. Chem.* **1970**, *21*, 315.

[9] Other mechanistic possibilities which we do not currently favor have been presented for the analogous silylketene thermolyses.[1]

[10] Soysa, H. S. D.; Jung, I. N.; Weber, W. P. *J. Organomet. Chem.* **1979**, *171*, 177.

Efficient Intramolecular 2 + 2 Photocycloaddition of Styrene Derivatives toward Cyclophanes

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The formation of 1,2-diphenylcyclobutane by the photocyclodimerization of styrene[1] has opposing demands with regard to the styrene concentration: the first dimerization step with a short-lived active species needs high concentration of styrene, whereas the second cyclization step requires dilute conditions to avoid intermolecular side reactions.

In order to overcome this monomer concentration effect by constraining the reactants into a single molecule,[2] α,ω-bis(vinylaryl)alkanes were treated under photoirradiation, which

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[1] (a) Mayo, F. R. *J. Am. Chem. Soc.* **1968**, *90*, 1289. (b) Brown, W. G. *J. Am. Chem. Soc.* **1968**, *90*, 1916. (c) Kricka, L. L.; Ledwith, A. *Synthesis* **1974**, 539. (d) Yamamoto, M.; Asanuma, T.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 53. (e) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 56. (f) Asanuma, T.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1975**, 608. (g) Asanuma, T.; Gotoh, T.; Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 485. (h) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Tetrahedron Lett.* **1981**, *22*, 2889. (i) Shirota, Y.; Nishikata, A.; Aoyama, T.; Saimatsu, J.; Oh, S.-C.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1984**, 64. (j) Tsuchida, A.; Yamamoto, M.; Nishijima, Y. *J. Chem. Soc., Perkin Trans. 2* **1986**, 239.

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