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On the Thermal Interconversion of Matrix-Isolated Dimethylsilylene and 2-Silapropene. Their Reactions with Oxygen Atom Donors

Charles A. Arrington,[1a,b] Robert West,[1c] and Josef Michl*[1a]

Departments of Chemistry, University of Utah
Salt Lake City, Utah 84112
and University of Wisconsin—Madison
Madison, Wisconsin 53706

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We have previously reported the matrix isolation of dimethylsilylene (**1**) and its photoconversion to 2-silapropene (**2**).[2] The latter compound dimerizes to dimethyl-1,3-disilacyclobutane upon warming to 50 K in argon, but forms insertion products characteristic of **1** when warmed to 100–120 K in 3-methylpentane in the presence of trapping agents such as triethylsilane. The simplest mechanism that accounts for these results is a rearrangement of **2** to **1** taking place near 100 K.[2]

However, there are now several reasons to doubt that this rearrangement is rapid at those temperatures: (i) in some pyrolyses which generate **2**, no evidence for **1** is detected;[3–5] (ii) ab initio MO calculations[8] on the parent silapropene–methylsilylene pair suggest that the rearrangement **1** $\rightleftarrows$ **2** is thermoneutral but has an activation energy of at least 40 kcal/mol, inconsistent with rapid rearrangement at 100 K; (iii) an ion cyclotron resonance study suggests that the rearrangement of **2** → **1** is about 28 kcal/mol endothermic[9] and therefore cannot be facile at 100 K.

Alternative mechanisms compatible with the experimental data are not immediately obvious. The proposal[10] that the structural assignment[2] of **2** needs to be revised was not particularly convincing from the outset and has become untenable as spectral evidence for other silenes has accumulated[3] and as the vibrational spectra of **2** were investigated in more detail.[11] Similarly, there is no doubt that the structure of **1** has been assigned correctly, on the basis of further spectroscopic study[3b,11] and by analogy to the properties of a large number of silylenes isolated in matrices since, including the direct observation of the formation of an isolable dimer from two of them.[12,13]

We have searched for trapping reagents that would be sufficiently reactive to react with **1** and/or **2** below 40 K in an argon matrix and wish to report here the results obtained with oxygen atom donors, which suggest a more complex alternative mechanism.

When **1** is produced by photolysis of $(Me_2Si)_6$ in an argon matrix doped with 0.5–1% N_2O, a new IR peak is observed at 1204 cm^{-1}. The UV and IR bands characteristic of **1** disappear when the matrix is warmed to 35 K overnight. The matrix remains pale yellow but its optical quality is insufficient for a reliable measurement of the weak visible absorption. During the warmup a new and much stronger peak appears at 1186 cm^{-1}; at high N_2O concentrations the 1204-cm^{-1} peak also is lost. In neat N_2O matrix (85 K) a broad band with four maxima between 1195 and 1208 cm^{-1} appears.

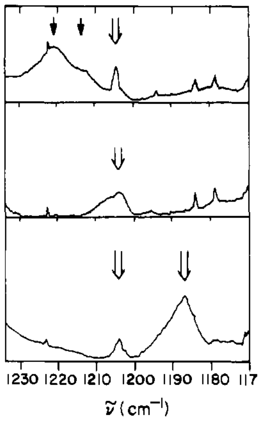


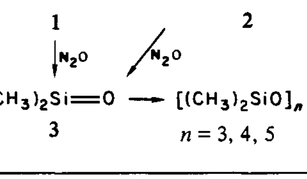
Figure 1. The 1170–1234-cm^{-1} region in the IR spectra in solid Ar/N_2O (200:1). Top, dimethylsilylene generated by photolysis of $(Me_2Si)_6$; bands at 1221 and 1213 cm^{-1} are due to **1**. Center, the same matrix but photolyzed at 450 nm to convert **1** to **2**. Bottom, the spectrum obtained by annealing either of the two matrices above at 35 K overnight. Bands at 1204 and 1186 cm^{-1} are believed to be due to **3** in various states of aggregation.

The new peaks in the 1200-cm^{-1} region do not appear when **1** or **2** is warmed in a matrix of pure argon or when dodecamethylcyclohexasilane is warmed in an argon matrix doped with N_2O. They do not belong to hexamethylcyclotrisiloxane, $(Me_2SiO)_3$, which is transparent in this region. They disappear upon further warming and are replaced by a new broad band at 1030 cm^{-1} in the region typical of Si–O stretching modes. This band is identical with that of an argon-matrix-isolated $(Me_2SiO)_3$. A GC-MS analysis of the warmup products revealed a single major product, identified as $(Me_2SiO)_3$, along with smaller amounts of $(Me_2SiO)_4$ and $(Me_2SiO)_5$.

Identical results are obtained with $^{15}N_2O$ as dopant, but with $N_2{}^{18}O$, the band at 1204 cm^{-1} is shifted to 1169 cm^{-1} and the isotropic analogue of the 1186-cm^{-1} band grows in under the broad band of the bending overtone of N_2O at 1152 cm^{-1}. Ethylene oxide as dopant gives rise to a new band at 1193 cm^{-1}, but $(CH_3)_3NO$, $(CH_3)_2SO$, and NO_2 did not produce any new bands in this region.

The experiments with N_2O as dopant were repeated with **2**. Strikingly, the same results were obtained (Figure 1): both **1** and **2** readily yield the same oxygen-containing trapping product as 35 K, a temperature at which they do not decay or interconvert measurably on the time scale of hours in the absence of dopant. This result suggests that the hydrogen shift needed to convert **2** to **1** does not occur spontaneously at low temperatures but is promoted by the act of trapping. Conceivably, then, a similar induction of the hydrogen shift by other trapping reagents may be responsible for the surprising results initially observed.[2]

As for the structure of the common trapping product obtaiend from both **1** and **2** with N_2O or ethylene oxide, the above evidence suggests dimethylsilanone (**3**) as the most likely candidate. It is known that generation of **1** in a fluid solution at room temperature in the presence of $(CH_3)_2SO$ yields trapping products characteristic of **3**.[14] To our knowledge, no organic silanones have been observed



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[1] (a) University of Utah. (b) On sabbatical leave from the Department of Chemistry, Furman University, Greenville, SC. (c) University of Wisconsin.

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before, but the Si=O vibrations of matrix-isolated SiO and SSiO and the antisymmetric stretch of matrix-isolated SiO_2 occur at 1224, 1265, and 1420 cm^{-1}, respectively,[15-17] and the Si=O stretching frequencies of Cl_2SiO and F_2SiO are 1240 cm^{-1} [17] and 1309 cm^{-1},[18] respectively. All of these results compare well with the bands observed for our trapping product at 1204 (presumably free) and 1186 cm^{-1} (presumably a weak complex with N_2O, not surprising for the undoubtedly highly polar Si=O bond). The ^{18}O isotope shifts of the Si=O stretch in Cl_2SiO and F_2SiO are 37 and 31 cm^{-1}, respectively; these can be compared with the value 35 cm^{-1} observed for our product.

An MNDO[19] calculation of vibrational frequencies and intensities of **3** predicts the Si=O stretch to fall at 1179 cm^{-1} for ^{16}O and 1143 cm^{-1} for ^{18}O; the calculated isotope shift is 36 cm^{-1}. The Si=O stretch is calculated to have the highest intensity of any vibrational mode above 400 cm^{-1}. An identification of additional vibrational transitions is clearly desirable but is hampered by the presence of the unreacted starting material, dodecamethylcyclohexasilane, and the byproduct, decamethylcyclopentasilane.

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Registry No. **1**, 6376-86-9; **2**, 38063-40-0; **3**, 47956-45-6.

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Halenaquinone, a Pentacyclic Polyketide from a Marine Sponge

Deborah M. Roll and Paul J. Scheuer*

Department of Chemistry, University of Hawaii at Manoa
Honolulu, Hawaii 96822

Gayle K. Matsumoto and Jon Clardy*

Department of Chemistry, Baker Laboratory
Cornell University, Ithaca, New York 14853

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Tropical marine sponges are a fertile source of secondary metabolites with diverse and often novel molecular architecture.[1] Many of these compounds also exhibit in vitro antimicrobial properties[2] and thus have generated much interest among synthetic and medicinal chemists, as well as among marine ecologists. A majority of known metabolites are terpenoid. Tyrosine and indole-derived structures constitute a second sizable group. Polyketides, on the other hand, are rare and had received little attention beyond research on the fatty acid composition of the Demospongiae[3,4] until the recent biochemical interest in membrane structure and function.[5,6] In this Communication we report isolation and structure of a new pentacyclic polyketide, which possesses in vitro antibiotic activity against *Staphylococcus aureus* and *Bacillus subtilis*.[7]

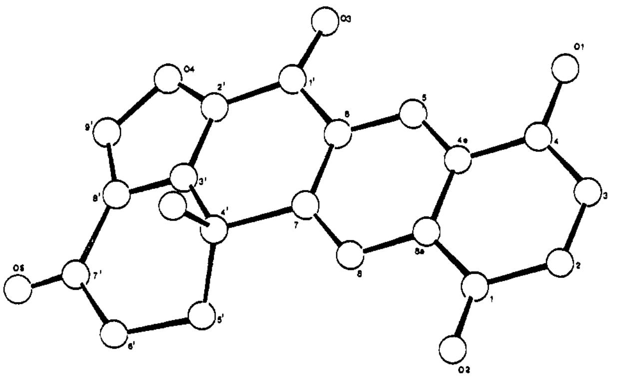
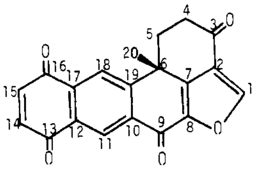


Figure 1. Computer-generated perspective drawing of halenaquinone. Hydrogens are omitted for clarity and no absolute configuration is implied.

Frozen *Xestospongia exigua*[8] was lyophilized and successively extracted at room temperature with hexane, benzene, dichloromethane, and ethanol. The residues were scanned by ^1H NMR. The benzene extract was chromatographed on Bio-Beads S-X8[9] (toluene) then Bio-Sil A[9] (CH_2Cl_2/EtOAc, 1:1) and finally by HPLC (Partisil M9,[10] C_6H_6/EtOAc, 2:1). The major metabolite was a yellow solid mp >250 °C dec, $[\alpha]^{25}{}_D$ +22.2° (*c* 0.124, CH_2Cl_2). A composition of $C_{20}H_{12}O_5$ was secured by high-resolution mass spectrometry (*m/z* 332.06847; calcd for $C_{20}H_{12}O_5$ 332.06847). Successive losses of CO and C_2H_2 from the molecular ion, an IR band at 1680 cm^{-1}, a two-proton singlet at δ 7.13 in the ^1H NMR spectrum, and four ^{13}C signals at δ 183.8(s), 183.3(s), 138.8(d), and 138.7(d) all pointed to a 2,3-unsubstituted-1,4-naphthoquinone, which was subsequently confirmed by treatment with Ac_2O, Zn, and Bu_4NBr, which readily yielded a leucodiacetate, mp 186–188 °C, $[\alpha]^{25}{}_D$ +62.1° (*c* 0.066, CH_2Cl_2),[11] and which we name halenaquinone (**1**).[12,13]



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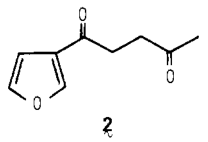

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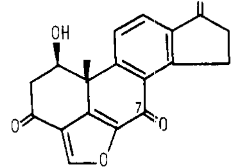

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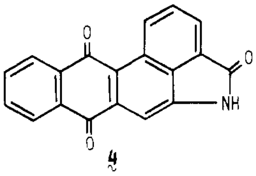

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(8) The sponge was first collected in Aug, 1977 in Palau, Western Caroline Islands by Dr. Mark Yunker and identified by Professor P. R. Bergquist, University of Auckland, N.Z. It was recollected in 1981 by Drs. Gary Schulte and Chris Ireland.
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(10) Whatman, Inc., Clifton, NJ.

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