Table III

Transition Temperatures for $ThC_2$[a]

| | Monoclinic–tetragonal transition | Tetragonal–cubic transition |
|---|---|---|
| Heating, °C | 1439 ± 24 | 1511 ± 28 |
| Cooling, °C | 1414 ± 29 | 1466 ± 16 |
| Hysteresis loop, °C | 25 | 45 |
| Average temp, °C | 1422 ± 28 | 1480 ± 21 |

[a] The data reported represent a recent reevaluation of the data in a similar table presented in ref 13. In no case has the temperature changed more than 5°.

proached. Over the limited composition range in which the monoclinic–tetragonal transition occurs, the width of the hysteresis loop apparently remains constant within the precision of the data. In the proposed phase diagram, this loop has been closed in the manner of a critical point to represent the fact that the tetragonal and monoclinic forms become indistinguishable (degenerate) at this point.

A phase diagram, constructed in accordance with the principles discussed for martensitic transformations, must be somewhat different from the usual eutectoid-type diagram. In Figure 14, the unusual features are the analog of the critical point referred to above and the fact that the two-phase regions do not reduce to a point at the terminal compositions. This unconventional behavior is in accord with the phase rule, as applied to binary systems exhibiting martensitic transformations.

An alternative construction of the diagram, in which there is no interaction between the miscibility gap and the martensitic transitions, has been considered. However, a rather strong argument against such a closed miscibility loop results from structural considerations. This type of construction would require complete miscibility of the two tetragonal phases between the consolute and the tetragonal–cubic transition temperature. Such complete miscibility would require a continuous transition from a structure with a $c/a$ ratio of 1.275 to one of 1.653. This has not been observed and seems quite improbable. Therefore, the closed miscibility loop construction has been rejected, and Figure 14[31] is proposed as the tentative phase diagram of the system with the admonition that it represents the system with the lattice strain energy being the third intensive thermodynamic variable.

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The electron microscope replicas were made by and examination and interpretation of the electron photomicrographs were performed by J. O. Gardner. Tom West carried out the analysis of numerous grains for uranium and thorium with the electron microprobe analyzer in an attempt to establish the presence of a second carbide phase.

Finally, the authors wish to thank A. W. Searcy, D. V. Ragone, J. H. Norman, and U. Merten for many long, helpful, and critical discussions and suggestions.

(31) Note Added in Proof.—Subsequent to the completion and submission of this paper for publication, a paper by Henney and Jones [J. Henney and J. W. S. Jones, Atomic Energy Research Establishment Report AERE-R-5093 (1965); to be published] has become available. While there is rather excellent agreement between their experimental data and ours, the interpretations result in phase diagrams which differ somewhat in details.

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# Notes

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## Synthesis of Methyldisilane by the Silent Electric Discharge of a Mixture of Silane and Dimethyl Ether[1]

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The present investigation was carried out in an attempt to prepare methyl and/or methoxy derivatives of the silicon hydrides by subjecting a mixture of $SiH_4$ and $(CH_3)_2O$ to a silent electric discharge in the same apparatus that had previously been used to convert $SiH_4$ to higher silanes.[2] Although a number of fractions were obtained by the gas chromatographic separation of the reaction products, all appeared to consist of inseparable mixtures, with the exception of one which contained relatively pure methyldisilane, $SiH_3SiH_2CH_3$, which was subsequently purified by distillation.

The mass and proton nuclear magnetic resonance spectra of $SiH_3SiH_2CH_3$ were consistent with its proposed structure. The proton resonance signal of the $SiH_2$ group was interesting in that it involved coupling between the protons on the $SiH_2$ group and the protons on both the $SiH_3$ and $CH_3$ groups. A quartet of quar-

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(1) This report is based on portions of a thesis submitted by Mansour Abedini to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 432 (1962).

tets was therefore to be expected for a first-order spectrum; but, either because of partial overlap of peaks or because of the small intensity of the two weakest peaks, a total of only 14 peaks could be observed. The resonance signals for the $SiH_3$ and $CH_3$ groups consisted of the expected triplets. Although the methyl group acts as an electron-releasing group in many organic compounds, it is of interest to note that in $SiH_3SiH_2CH_3$ it *acts* as if it were an electron-withdrawing group in that it causes the $SiH_2$ resonance signal to fall at a considerably lower field (0.50 ppm lower) than the $SiH_3$ signal. This ($\delta SiH_3 - \delta SiH_2$) value is similar in both magnitude and sign to the ($\delta SiH_3 - \delta SiH_2$) value of 0.71 ppm observed for $Si_2H_5Br$.[3] In both $SiH_3SiH_2CH_3$ and $SiH_3SiH_2Br$ the proton chemical shift of the $SiH_2$ groups falls to low field of the proton signal in $Si_2H_6$.[3] Whether these downfield shifts are caused primarily by simple inductive effects due to replacement of a hydrogen (electronegativity, 2.1) in $H_3SiSiH_3$ by a methyl group (electronegativity, 2.64[4]) or by anisotropic and related effects is not known; however, it is interesting that the shifts are in qualitative agreement with those which might be expected from the above recently reported value for the electronegativity of the methyl group[4] and the electronegativity of bromine (2.8). It may be significant that similar effects, which are also consistent with the methyl group *acting* as if it had had electron-withdrawing properties, can be observed in other hydrides. Thus, replacement of a hydrogen atom by a methyl group in the series $H_xSi(CH_3)_{4-x}$,[5] $H_xGe(CH_3)_{4-x}$,[5] $H_xSn(CH_3)_{4-x}$,[6] $H_xP(CH_3)_{3-x}$,[7] and $H_xAs(CH_3)_{3-x}$[8] in all cases brings about a progressive, although not necessarily equal, downfield shift of the remaining M–H protons (M = Si, Ge, Sn, P, As).

In an unconfirmed report[9] it has been claimed that $SiH_3SiH_2CH_3$ is formed together with $CH_3SiH_3$ when $CH_3Cl$ is treated with a liquid ammonia solution of $KSiH_3$ which was believed to contain some $KSi_2H_5$. This solution was prepared by the reaction of $Si_2H_6$ with a solution of potassium in liquid $NH_3$. The $SiH_3SiH_2CH_3$ obtained was reported to boil at 28.2° (Trouton's constant 14.0 cal $deg^{-1}$ $mole^{-1}$) and to have no sharp freezing point but to turn to a glassy solid at low temperatures. The present investigation shows that this material may well not have been $SiH_3SiH_2CH_3$, since the pure $SiH_3SiH_2CH_3$ prepared in this research, the structure of which is completely consistent with its proton nuclear magnetic resonance spectrum, boiled at 16.6° and melted sharply at −134.9°. Unlike the previously reported material, it was spontaneously inflammable in air, like other compounds containing the $Si_2H_5$ group.[10,11] It also does not seem likely that the previously reported $SiH_3SiH_2CH_3$ (bp 28.2°) was the isomeric species $CH_2(SiH_3)_2$ (bp 15.3° (770 mm)[12]).

### Experimental Section

All work was carried out in a borosilicate (Pyrex) glass vacuum system. All apparatus, including that used for the discharge reaction,[2,13] instruments, and techniques were identical with those previously described.[10,11,14] The mass spectrum was measured by means of a Consolidated Electrodynamics Corp. Model 21-130 mass spectrometer operating at an ionizing voltage of 76.0 v and at an ionization current of 20 ma. The proton nuclear magnetic resonance spectrum was recorded by means of an HR60 Varian Associates spectrometer, Model 4300D, with flux stabilizer, operated at 60 Mc/sec at room temperature. Infrared spectra were obtained with a Perkin-Elmer 137B infrared spectrometer using a 10-cm gas cell fitted with KBr windows. Gas chromatographic separations were carried out by means of a column (21 ft, 0.5-in. diameter, packed with Dow Corning 702 silicone oil dispersed on 60–80 mesh acid-washed firebrick in a 1:5 weight ratio) attached to a Perkin-Elmer vapor fractometer (Model 154D). The unit was operated at a helium pressure of 25 psi and at a flow rate of 490 ml $min^{-1}$.

Silane (mol wt found 31.8, calcd 32.12; confirmed by infrared spectrum[15]) was prepared by the $LiAlH_4$ reduction of $SiCl_4$. Commercial $(CH_3)_2O$ was used without further purification.

In a typical experiment, a mixture of $SiH_4$ (0.642 g, 20.0 mmoles) and $(CH_3)_2O$ (1.13 g, 23.5 mmoles) was circulated through the ozonizer (connected to a 7500-v neon sign transformer), by means of an automatic Toepler pump. The mixture was passed through the apparatus for 6 hr at a pumping rate of 500 ml $min^{-1}$. The initial gas pressure in the apparatus was 150 mm. Because of the liberation of considerable quantities of hydrogen, this pressure had increased to 170 mm at the end of the experiment. The gas issuing from the ozonizer was continuously passed through two traps held at −96° to remove products having a lower volatility than the unused reactants. At the conclusion of the experiment, hydrogen was removed by pumping all volatile material through five traps held at −196° in which the hydrogen did not condense. The volatile material remaining was then passed through a trap held at −112° in which most of the products, but not unreacted $SiH_4$ (0.10 g, 3.1 mmoles; identified by infrared spectrum[15]), unreacted $(CH_3)_2O$ (identified by infrared spectrum[16]), and a small quantity of $Si_2H_6$ (identified by infrared spectrum[17]), condensed. The condensate in the −112° trap was then passed through the gas chromatographic column. Several fractions were obtained. Those identified were $Si_3H_8$ (identified by infrared spectrum[2]) and $SiH_3SiH_2CH_3$ containing some $(CH_3)_2O$ (retention time 16.5 min). The latter fraction was distilled in a low-temperature distilling column.[18] The fraction volatilizing at −95° was pure $SiH_3SiH_2CH_3$ (~0.06 g, ~0.8 mmole; mol wt found 76.0, calcd 76.25).

A freshly distilled sample of $SiH_3SiH_2CH_3$ (0.01241 g, 0.1628 mmole; mol wt found 76.8, calcd 76.25; vapor pressure at

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