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Reactions of Silicon Atoms with Methyl Iodide: Direct Synthesis of Methyliodosilanes at Low Temperature and in Absence of Any Catalyst[1]

Günther Maier* and Jörg Glatthaar

Institut für Organische Chemie der Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany

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Co-condensation of thermally generated silicon atoms with methyl iodide (**1**) at liquid nitrogen temperature (77 K) offers an access to dimethyldiiodosilane (**2**), methyltriiodosilane (**3**), and 1,2-dimethyl-1,1,2,2-tetraiododisilane (**4**). These low-temperature reactions between atomic silicon and solid methyl iodide occur spontaneously in the absence of any catalyst. The mechanism of this process and its relevance to the Rochow−Müller synthesis is discussed.

Introduction

In a recent essay Seyferth[2] described the enormous importance of the "direct synthesis" of dimethyldichlorosilane by reaction of a silicon/copper alloy with methyl chloride.[3,4] At the same time he points out that even today, 66 years after its discovery in 1940, the mechanism of this process is still not fully understood. It was our hope that investigation of the behavior of Si atoms in a matrix may perhaps throw some light upon the fundamental steps in the Rochow−Müller (R−M) synthesis. This is indeed the case.[5]

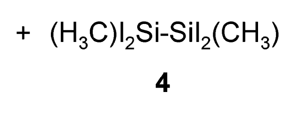
In our earlier study it already became obvious that methyl iodide may be an ideal candidate for a thermal "direct synthesis" in condensed phase at low temperature and in the absence of any catalyst.[5] The realization of this expectation is described in the present paper. Our goal, to expand our analytical matrix isolation studies to a more preparative usable application, has been reached.

Experimental Section

The peculiar reactivity of silicon atoms with methyl iodide (**1**) compared to the other methyl halides has been revealed before.[5] In an argon matrix at 10 K all methyl halides form in the initial step triplet *n*-adducts of type **T-5**. In the case of the fluoride, chloride, or bromide the subsequent transformation into the corresponding singlet silylenes requires photoactivation. But upon reaction of methyl iodide (**1**) with Si atoms in argon at 10 K, instead of *n*-adduct **T-5** only singlet methyliodosilylene **S-8** is observed. This fact indicates that *n*-adduct **T-5** isomerizes (first insertion) spontaneously, without photochemical activation, to silylene **S-8**. This view was supported by another experiment: If **1** is co-condensed with silicon atoms at 40 K under simultaneous irradiation with 366 nm light, the only detectable product is dimethyldiiodosilane (**2**) (product of a second insertion).[5] So the question arose, whether the insertion of silylene **S-8** into the Si−I bond of an additional methyl iodide molecule **1** can be forced to occur in the absence of photochemical excitation by switching to a higher (above 40 K) temperature instead. As already briefly mentioned,[5] the IR bands of **2** could indeed be detected when pure methyl iodide (**1**) and Si atoms were co-condensed at 80 K without irradiation onto the cold end of a helium closed-cycle refrigeration system. This observation was a strong hint that it should be possible to expand the matrix-spectroscopic studies carried out so far and to prepare dimethyldiiodosilane (**2**) in higher quantities by using more practical techniques. As is shown below, this intention can be realized if silicon is evaporated in a newly constructed apparatus (Figure 1), which allows co-condensation at liquid nitrogen temperature (77 K).

For the production of silicon atoms a strip cut out from a p-type doped silicon wafer (Wacker) was heated resistively. Under these conditions the surface temperature was 1350−1380 °C. The silicon atoms were co-condensed with methyl iodide (**1**) in high vacuum onto the surface of a vessel, which was cooled with liquid nitrogen. A yellow solid layer was formed on the inner side of the flask. After 3 h the co-condensation was finished. Upon removal of the cooling bath, the yellow color disappeared immediately. The apparatus was flushed with argon. A slightly yellow liquid gathered at the bottom of the vessel. Sampling had to occur in the complete absence of air and moisture. The products were identified by comparison with authentic samples (gas chromatography, GC/MS, and NMR spectroscopy).

The isolated liquid contained mainly unreacted methyl iodide (**1**). In addition dimethyldiiodosilane (**2**), methyltriiodosilane (**3**), and 1,2-dimethyl-1,1,2,2-tetraiododisilane (**4**) could be identified as reaction products.



$$\cdot\ddot{\mathrm{Si}}\cdot + \underset{\mathbf{1}}{\mathrm{H_3C{-}I}} \xrightarrow{77\,\mathrm{K}} \underset{\mathbf{2}}{\mathrm{(H_3C)_2SiI_2}} + \underset{\mathbf{3}}{\mathrm{H_3CSiI_3}} + \underset{\mathbf{4}}{\mathrm{(H_3C)I_2Si{-}SiI_2(CH_3)}}$$

For comparison dimethyldiiodosilane (**2**) was prepared separately following the procedure of Kummer and Fritz by the reaction of

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* Corresponding author. Fax: (+49)641-99-34309. E-mail: Guenther.Maier@org.chemie.uni-giessen.de.

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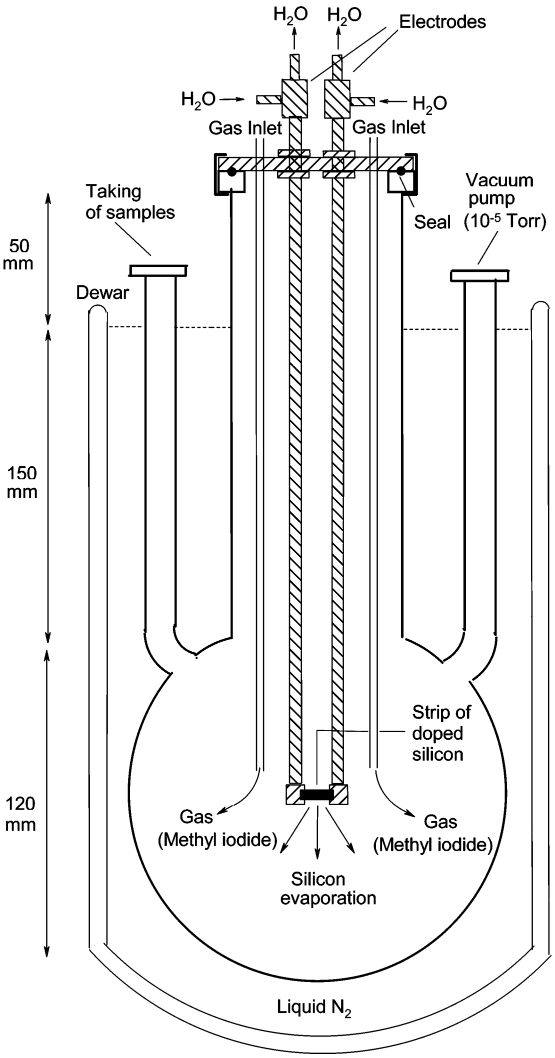

Figure 1. Apparatus for the reaction of silicon atoms with solid methyl iodide (**1**) at liquid nitrogen temperature.

diphenyldimethylsilane with hydrogen iodide.[6] Authentic methyltriiodosilane (**3**) and 1,2-dimethyl-1,1,2,2-tetraiododisilane (**4**) were synthesized according to the Ruff method[7] using a variation mentioned by Kummer et al.,[8] consisting in the reaction of the corresponding chlorosilanes with ethylamine and subsequent cleavage of the Si$-$N bonds of the aminosilanes thus formed with hydrogen iodide. According to our experience, it is better to use toluene as solvent instead of petroleum ether.

The NMR spectrum of the product mixture showed in addition to the signal due to methyl iodide (**1**) the signals due to **2**, **3**, and **4**. The assignments were based on comparison with the spectra of authentic samples. The spectral data for **2** (^{1}H: $\delta = 1.6$; ^{13}C: $\delta = 12.8$; ^{29}Si: $\delta = -34.8$) and **4** (^{1}H: $\delta = 1.7$; ^{13}C: $\delta = 6.0$; ^{29}Si: $\delta = -52.5$) corresponded to the values given in the literature.[8−10] The chemical shifts attributed to **3** (^{1}H: $\delta = 2.4$; ^{13}C: $\delta = 20.9$; ^{29}Si: $\delta = -143.5$) were in accordance with the reported ^{13}C value ($\delta = 21.10$),[9] but differed remarkably with the published chemical shifts of the proton (^{1}H: $\delta = 0.91$)[10] and silicon spectra (^{29}Si: $\delta = -17.96$).[10] However, on the basis of the mass spectrum and the synthetic route for the authentic sample the identity of **3** can be taken for granted. It was found that the ^{1}H and ^{13}C signals attributed to **2**, **3**, and **4** in the NMR spectra of the reaction mixture increased upon addition of separately prepared authentic **2**, **3**, or **4**. As far as the discrepancies with the ^{1}H and ^{29}Si NMR data reported for **3**[10] are concerned, we have to suppose that the literature values are incorrect.

The gas chromatographic analysis of the volatile products was carried out after bulb-to-bulb distillation of the collected pyrolysate. In the gas chromatogram (silylated polysiloxane column) three peaks could be detected, belonging to unreacted methyl iodide (**1**), dimethyldiiodosilane (**2**), and methyltriiodosilane (**3**). The characteristic fragmentation pattern in the mass spectra of **2** ($m/e = 312$, 297, 158, 128) and **3** ($m/e = 424$, 409, 297, 128) agreed with those of the authentic samples of **2**[6] and **3**.[7]

Iodosilanes **2**−**4**, and this is especially true for methyltriiodosilane (**3**), are extremely sensitive toward moisture. As a result, addition of water to a solution of the co-condensate results in instantaneous formation of a gelatinous precipitate of cross-linked polysiloxanes. The ATR spectrum of the isolated solid showed the typical IR bands of a methylated polysiloxane. Gas chromatographic analysis of the filtrate indicated the presence of the oligomers of dimethylsilanone (characteristic signals for the cyclic siloxanes, in technical terms "D3−D6", containing six-, eight-, ten-, or twelve-membered rings).

The yields of **2**, **3**, and **4** depend on the ratio of Si atoms to methyl iodide (**1**). In the case of high Si concentrations (evaporation of 11.2 mg of Si; ratio of Si atoms:methyl iodide (**1**) ≤ 1:10) the total yield of methyliodosilanes is small and the relative amount of isolated dimethyldiodosilane (**2**) is rather low (4 mole % **2**, 6 mole % **3** an 1 mole % **4**; determined NMR spectroscopically). Under these conditions brownish spots (coagulated silicon) were detected. In an experiment using a ratio of Si atoms:methyl iodide (**1**) = 1:20 the yields were 9 mole % **2**, 18 mole % **3**, and 2 mole % **4** based on the amount of vaporized silicon (10.0 mg). Further experiments showed that with even lower concentrations of Si atoms the total yield of isolated methyliodosilanes still increased and the relative amount of dimethyldiiodosilane (**2**) reached a maximum. If a ratio of Si atoms (16.4 mg):methyl iodide (**1**) = 1:100 was used, the yields were 66 mole % **2**, 10 mole % **3**, and 8 mole % **4**. In none of the experiments could further silanes be observed.

Similar reactions carried out using methyl chloride or methyl bromide in place of methyl iodide failed.

In a crucial experiment we were able to show that the presence of silicon atoms is the prerequisite for the reactions described above. As is known from MS studies, vaporized silicon consists of roughly 98% Si atoms. Si$_n$ clusters of the size $n = 2-4$ are only minor components.[11] In this context it is important to know that no reaction occurred if the following experimental procedure was applied: condensation of the silicon atoms on the cold surface (formation of a silicon layer) followed by subsequent condensation of methyl iodide (**1**).

Discussion

In spite of the fact that the conditions are completely different, the results of the reaction between silicon atoms and solid methyl iodide (**1**) on one hand and the technical R−M synthesis on the other hand are in principle the same. Analogous to the formation of **2**, **3**, and **4** from **1** at 77 K, the industrial "direct synthesis", which involves reaction of the Si/Cu alloy with methyl chloride, produces dimethyldichlorosilane, methyltrichlorosilane, and *sym* dimethyltetrachlorodisilane as the main products.[4]

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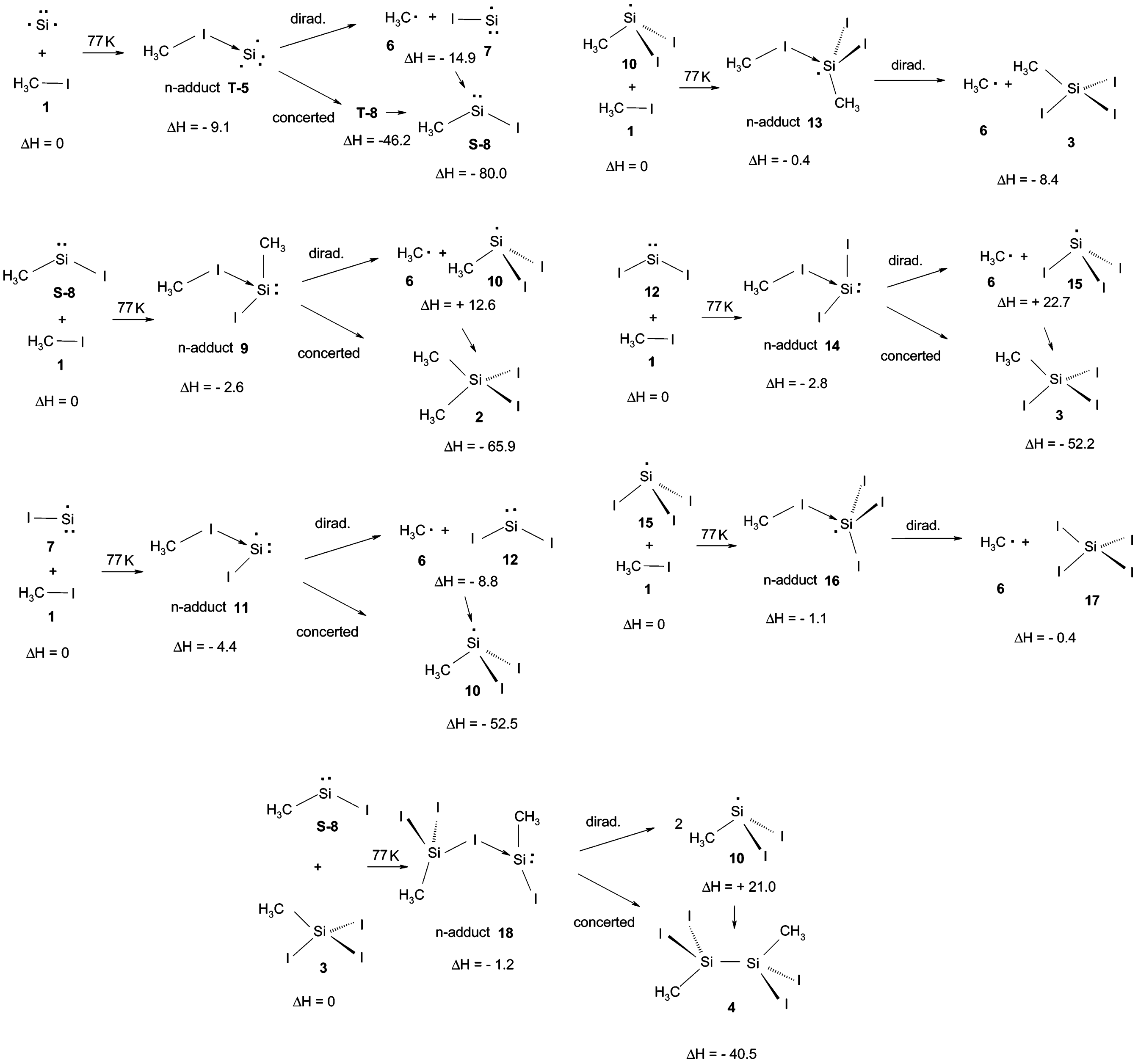
Scheme 1. Calculations Concerning the Reaction Mechanism of the Direct Synthesis of Iodosilanes 2, 3, and 4[a]



[a] Relative energies in kcal mol^{-1}.

At the beginning of his studies Rochow had tried to use methyl iodide (**1**) as starting material.[3,12] In view of the high temperature applied in this process, it is no surprise that he states in a footnote:[3] "That methyl iodosilanes also may be made by the action of methyl iodide on sintered copper-silicon pellets at 300 °C has been shown by hydrolyzing the products from such a reaction and demonstrating the existence of methyl silicone by analysis. Decomposition of free iodine and the formation of silicon tetraiodide probably are responsible for the poor yields which were obtained." Other alkyl iodides gave no better results.[12,13]

The use of Si atoms has the advantage that the reaction with methyl iodide (**1**) already occurs at very low temperature, at which the formed iodosilanes are thermally stable. But other points remain mysterious. Why does the reaction described above only work with methyl iodide, but not with the other methyl halides? What is the origin for the high yield of methyltriiodosilane (**3**)? An answer can only be given on the basis of theoretical calculations.[5]

Calculations. In order to obtain an overview of the relevant potential energy surfaces not considered before,[5] and to gain detailed information on the mechanism of the direct synthesis using methyl iodide (**1**), several additional stationary points (minima and connecting transition states) were calculated with the SDD basis set and the B3LYP functional using the Gaussian package of programs.[14]

Reaction Mechanism. According to our earlier matrix isolation studies,[5] a silicon atom is attacked by methyl iodide (**1**), resulting in the formation of *n*-adduct **T-5** (Scheme 1). Calculations show that this step is exothermic ($\Delta H_r = -9.1$ kcal mol^{-1}). The spontaneous insertion reaction **T-5** → **S-8** probably follows a diradical type pathway via the combination of the methyl radical (**6**) and silicon monoiodide (**7**). The corresponding transition state $\mathbf{TS}_{\mathbf{T\text{-}5}\rightarrow\mathbf{7+6}}$ is much lower in energy

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[12] See also ref 4a, pp 188 and 274.

[13] Kanner, B.; Lewis, K. M. In ref 4b, p 34.

Table 1. Calculated Absolute Energies, Zero-Point Energies, and S^2 Values of Species 1−18 (with B3LYP/6-311+G for C, H, Si and with Extra Basis Set SDD for I)**

species (point group, state)	energy [hartrees]	energy + ZPE [hartrees]	ZPE [hartrees]	S^2
Si^3 (^{3}P)	−289.39417	−289.39417	0.00000	2.0020
1 (C_1, $^1A_1$)	−51.34342	−51.30689	0.03652	0.0000
2 (C_s, $^1A'$)	−392.31641	−392.24060	0.07581	0.0000
3 (C_1, $^1A_1$)	−363.82279	−363.78274	0.04005	0.0000
4 (C_i, ^1A_g)	−704.75529	−704.67598	0.07932	0.0000
T-5 (C_1, $^3A_1$)	−340.75234	−340.71554	0.03680	2.0038
6 (D_{3h}, $^2A_2''$)	−39.85613	−39.82652	0.02961	0.7534
7 ($C_{\infty v}$, $^2\Sigma^+$)	−300.89897	−300.89823	0.00074	0.7532
T-8 (C_1, $^3A_1$)	−340.81147	−340.77472	0.03675	2.0029
S-8 (C_1, $^1A_1$)	−340.86476	−340.82863	0.03613	0.0000
9 (C_1, $^1A_1$)	−392.21366	−392.13970	0.07396	0.0000
10 (C_1, $^2A_1$)	−352.32733	−352.28893	0.03841	0.7524
11 (C_1, $^2A_1$)	−352.25017	−352.21220	0.03797	0.7535
12 (C_{2v}, $^1A_1$)	−312.39425	−312.39265	0.00160	0.0000
13 (C_1, $^2A_1$)	−403.67161	−403.59642	0.07519	0.7525
14 (C_1, $^1A_1$)	−363.74297	−363.70403	0.03894	0.0000
15 (C_{3v}, $^2A_1$)	−323.83959	−323.83689	0.00271	0.7541
16 (C_1, $^2A_1$)	−375.18507	−375.14548	0.03959	0.7539
17 (T_d, $^1A_1$)	−335.32177	−335.31791	0.00386	0.0000
18 (C_1, $^1A_1$)	−704.69001	−704.61330	0.07681	0.0000
$\mathbf{TS}_{\mathbf{T\text{-}5}\rightarrow\mathbf{7+6}}$ (C_1, $^3A_1$)	−340.74686	−340.71270	0.03416	2.0274
$\mathbf{TS}_{\mathbf{T\text{-}5}\rightarrow\mathbf{T\text{-}8}}$ (C_1, $^3A_1$)	−340.72587	−340.69048	0.03539	2.0050
$\mathbf{TS}_{\mathbf{9}\rightarrow\mathbf{2}}$ (C_1, $^1A_1$)	−392.15963	−392.08696	0.07267	0.0000
$\mathbf{TS}_{\mathbf{11}\rightarrow\mathbf{12+6}}$ (C_1, $^2A_1$)	−352.24223	−352.20714	0.03509	0.7804
$\mathbf{TS}_{\mathbf{13}\rightarrow\mathbf{3+6}}$ (C_1, $^2A_1$)	−403.66791	−403.59407	0.07384	0.7664
$\mathbf{TS}_{\mathbf{14}\rightarrow\mathbf{3}}$ (C_1, $^1A_1$)	−363.67802	−363.64097	0.03705	0.0000
$\mathbf{TS}_{\mathbf{16}\rightarrow\mathbf{17+6}}$ (C_1, $^2A_1$)	−375.17440	−375.13717	0.03723	0.7702
$\mathbf{TS}_{\mathbf{18}\rightarrow\mathbf{4}}$ (C_1, $^1A_1$)	−704.67214	−704.59452	0.07762	0.0000

(E_a = 1.8 kcal mol^{-1}) than the barrier for the concerted conversion of **T-5** to the triplet silylene **T-8** ($\mathbf{TS}_{\mathbf{T\text{-}5}\rightarrow\mathbf{T\text{-}8}}$; E_a = 25.7 kcal mol^{-1}). So one has to assume that the singlet silylene **S-8** is formed via the fragmentation/recombination process **T-5** → **6** + **7** → **S-8**.

The surprisingly easy formation of a methyl radical (**6**) by attack of a low-valent silicon species on methyl iodide **1** is typical for *n*-adducts with triplet or doublet multiplicity (Scheme 1). For instance, the radical type fragmentation of **11** needs an activation energy of only 3.2 kcal mol^{-1} ($\mathbf{TS}_{\mathbf{11}\rightarrow\mathbf{12+6}}$). Similar values are calculated for **13** ($\mathbf{TS}_{\mathbf{13}\rightarrow\mathbf{3+6}}$; E_a = 1.5 kcal mol^{-1}) and **16** ($\mathbf{TS}_{\mathbf{14}\rightarrow\mathbf{3}}$; E_a = 5.2 kcal mol^{-1}). The barriers for the concerted C−I insertion reactions of the singlet *n*-adducts **9** and **14** are much higher ($\mathbf{TS}_{\mathbf{9}\rightarrow\mathbf{2}}$, E_a = 30.4 kcal mol^{-1}; $\mathbf{TS}_{\mathbf{14}\rightarrow\mathbf{3}}$, E_a = 36.7 kcal mol^{-1}). Interestingly, the Si−I insertion in the case of *n*-adduct **18** is predicted to be only 11.8 kcal mol^{-1} ($\mathbf{TS}_{\mathbf{18}\rightarrow\mathbf{4}}$), allowing in the case of formation of disilane **4** not only the diradical but also the concerted pathway.

Since silylene **S-8** is embedded in solid methyl iodide, the initially formed iodomethylsilylene **S-8** is not free but stabilized as the donor−acceptor complex **9**. In a process similar to the transformation **T-5** → **S-8** a second insertion leading from **9** to the desired dimethyldiiodosilane (**2**) can occur. Scheme 1 also offers an explanation for the observation of the additional products **3** and **4**. Siliconmonoiodide (**7**) may generate methyldiiodosilyl radical (**10**), which can be regarded as a precursor not only for dimethyldiiodosilane (**2**) but also for methyltriiodosilane (**3**) and 1,2-dimethyl-1,1,2,2-tetraiododisilane (**4**).

Conclusion

A thermal "direct synthesis" of a dialkyldihalosilane at low temperature in the absence of a catalyst is possible if the following prerequisites are fulfilled: (a) The grain size of the reacting silicon must be as small as possible. The extreme is reached with silicon atoms. (b) The alkyl halide must form an *n*-adduct of type **T-5**, which must be thermodynamically equal or lower in energy than the sum of the two partners. (c) The *n*-adduct must be kinetically unstable, in order to allow a fast reaction (first insertion) under formation of the corresponding silylene. For instance, the weak C−I bond is preferred compared to the other C−Hal bonds. (d) The initially formed silylene should be able to form an acceptor−donor complex of type **9**, which again is thermodynamically equal or lower in energy than the sum of the two components. (e) This complex also must be kinetically unstable, in order to allow a fast formation (second insertion) of the final dialkyldihalosilane. Once more the weak C−I bond is better than another C−X bond. To sum up, generally a successful "direct synthesis" at low temperature can be expected if silicon atoms are treated with substrates RX of high nucleophilicity, which form *n*-adducts and silylene complexes with weak C−X bonds.

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Supporting Information Available: Includes structural features (ISIS Draw sketch files) and Gaussian output archives (Gaussian 03, Revision D.02) of the calculated minima of molecules **1**−**18** and related transitions states (see Table 1). This material is available free of charge via the Internet at http://pubs.acs.org.

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