

Probing the Mechanism of Aldehyde Addition to a Disilene and Two Silenes: Solvent Effects

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Summary: The effect of changing the solvent from a hydrocarbon to acetonitrile on the mechanism of the addition of aldehydes to a disilene and two silenes was investigated. The products of the reaction between $Mes_2Si=CH(CH_2-t-Bu)$ and acetonitrile were characterized.

Since the isolation of the first stable disilene¹ and silene² in the early 1980s, the chemistry of these important compounds has been studied in an effort to understand their reactivity, particularly in comparison to their alkene analogues. In general, (di)silenes react more rapidly than alkenes with a variety of reagents, making them excellent starting materials for the synthesis of many silicon-containing compounds,^{3,4} including polymers.⁵

The addition of ketones and aldehydes to group 14 (di)metallenes has been a key reaction in the development of the chemistry of this class of compounds.³ (Di)silenes react

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The addition of 1 to Mes₂Si=SiMes₂ (2)^{7b} in hexanes leads to two products, the cis,trans-diene **5** and oxadisilacycloheptene **6** in a 1:1 ratio (Scheme 1).^{7b} The structures of compounds **5** and **6** are completely consistent with the initial formation of a 1,4-biradical intermediate. Similarly, the addition of **1** to (Me₃Si)₂Si=C(OSiMe₃)R^{7a} (R = *t*-Bu (**3a**), R = 1-Ad (**3b**)) in benzene proceeds through a 1,4biradical intermediate which, in both cases, forms the cis, trans-diene **7** as the major product (Scheme 2).^{7a} A diastereomeric mixture of two siloxetanes (**8**) and trace amounts of diastereomeric acylsilanes (**9**) were also formed in the addition of **1** to silenes **3a**,b.^{7a} In contrast, the addition of **1** to Mes₂Si=CH(CH₂-*t*-Bu)^{7a} (**4**) in benzene proceeds through a 1,4-zwitterionic intermediate, which results in the formation of three diastereomers of siloxetane **10** and ester **11** (Scheme 3).^{7a} The major product, vinylsilane **12**, is presumably formed via an ene reaction.

The addition of formaldehyde to the parent (di)silenes, $H_2Si=SiH_2$ and $H_2Si=CH_2$, has also been examined using density functional theory (DFT) in an effort to evaluate the most likely mechanistic pathway for the formation of (di)siloxetanes from the reaction of formaldehyde with the parent (di)silene (Scheme 4).⁸ For the addition of formaldehyde

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Scheme 2. Addition of Aldehyde 1 to Silenes 3a,b in Benzene



Scheme 3. Addition of Aldehyde 1 to Silene 4 in Benzene



to $H_2Si=SiH_2$ in the gas phase, two possible zwitterionic pathways and a biradical pathway were located; the biradical pathway was the most energetically favorable.⁸ For the addition of formaldehyde to $H_2Si=CH_2$ in the gas phase, three possible pathways (biradical, zwitterionic, and concerted) were identified.⁸ The biradical and zwitterionic pathways were competitive; the calculated free energy barrier for the concerted pathway was too high to be competitive with the pathways involving an intermediate. Given that the biradical and zwitterionic pathways are competitive, substituent effects may be critical in determining the operative mechanism in a given system. Indeed,

Scheme 4. Addition of Formaldehyde to Disilene and Silene



as illustrated in Schemes 2 and 3, we have shown experimentally that silenes with different substituents may indeed follow different reaction pathways.^{7a}

The influence of various solvents of increasing dielectric constant on the energetics of the reaction was also considered in the computational study.8 Specifically, the influence of cyclohexane, acetone, acetonitrile, and water, which have dielectric constants of 2.02, 20.56, 35.94, and 78.36, respectively,¹⁰ was examined. Although water and acetone are known to react with (di)silenes, these solvents were selected to include solvents with a wide range of dielectric constants. As the dielectric constant of the solvent increased, the energy difference between the zwitterionic and biradical pathways decreased in the addition of formaldehyde to H₂Si=SiH₂; a concerted pathway was not located. For all solvents considered, the biradical pathway remained the most energetically favorable pathway. In the addition of formaldehyde to H₂Si=CH₂, as the dielectric constant of the solvent increased, the zwitterionic pathway became slightly favored over the biradical pathway; the concerted pathway remained highest in energy.8 The influence of solvent polarity on the kinetics of the reaction between the transient Ph₂Si=CH(CH₂-t-Bu) and acetone has been examined experimentally;6b changing the solvent from hexane to acetonitrile decreased the rate constant of the reaction by a factor of 3, as would be expected by a small increase in the destabilization of the transition state on going from a polarized intermediate complex to products. A polarized intermediate is believed to be involved in both hexane and acetonitrile.

In this study, we have repeated the addition of aldehyde 1 to disilene 2, silene 3a, and silene 4 in a solvent with a relatively high dielectric constant and compared the structures of the products with those obtained in hydrocarbon solvents. The goal was to determine if the reaction pathways would be significantly influenced by the dielectric constant of the solvent, as suggested by the computational study. The mechanism of the addition of 1 to silene 4 in benzene is zwitterionic in nature,^{7a} and therefore, conducting this reaction in a solvent with a higher dielectric constant would likely not alter the mechanism of addition. However, since the addition of 1 to silene 4 is quite complex and results in the formation of five compounds in hydrocarbon solvent, the product ratios may show a solvent dependency.

A suitable solvent, one with a high dielectric constant which would not react or complex with the (di)silene being examined, was needed. Although water, alcohols, and carbonyl compounds have high dielectric constants, these compounds react rapidly with (di)silenes, and therefore, common solvents

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Scheme 5. Mechanism of Addition of Aldehyde 1 to Disilene 2



such as methanol, ethanol, and acetone are inappropriate for use in this experimental study. Furthermore, ether solvents are also undesirable, as they may alter the reactivity of the silene by complexation.^{6c} Acetonitrile, on the other hand, has a relatively high dielectric constant (35.94) and is frequently used as a fairly inert solvent in the kinetic studies of a variety of silenes.^{6a-d} Although the addition of nitriles to some disilenes has been reported,¹¹ there have been no reports in the literature of the addition of acetonitrile to Mes₂Si=SiMes₂. Therefore, acetonitrile was chosen as an appropriate aprotic solvent with relatively high polarity for this study.

Results and Discussion

To study the addition of aldehyde 1 to disilene 2 in acetonitrile, 2, a bright yellow solid, was generated by the photolysis of $Mes_2Si(SiMe_3)_2$ at -70 °C in hexanes.^{1,7b} The hexanes were then removed and replaced with CH₃CN. Following the addition of 1 to 2, the reaction mixture was stirred for 24 h to give a colorless solution and a white solid. The ¹H NMR spectrum of the crude reaction mixture revealed the presence of cis, transdiene 5 and oxadisilacycloheptene 6 in a 1.6:1 ratio, which is similar to the ratio of products obtained in hexanes.^{7b} Since compounds 5 and 6 are both derived from ring opening of the cyclopropyl ring of aldehyde 1, 1 adds to 2 in CH₃CN via a mechanism which passes through a 1,4-biradical intermediate. Furthermore, since the ratio of 5 to 6 was found to be similar to the ratio obtained in hexanes, CH₃CN does not significantly alter the rate of cyclization or disproportionation of the 1,7biradical intermediate (Scheme 5). Thus, we conclude that the solvent does not alter the broad features of the mechanism of the addition of aldehyde 1 to disilene 2.

The addition of aldehyde 1 to silene 3a in CH₃CN was also examined. Silene 3a was prepared by irradiating a C₆D₆ solution of an acyltris(trimethylsilyl)silane; the progress of the reaction was monitored by ¹H NMR spectroscopy. ^{7a} The formation of silene 3a and its head-to-head dimer was confirmed by a comparison of the observed chemical shifts to those reported in the literature. ¹² At ~73% conversion of the precursor to silene and dimer, the solvent was removed and a solution of 1 in CH₃CN was added. Upon the addition of 1 to 3a, the pale yellow color of the solution faded within minutes. A white solid, presumably the dimer of 3a, ¹² was insoluble in CH₃CN at room temperature; however, the solid dissolved when the reaction

Scheme 6. Addition of Acetonitrile to Silene 4



mixture was heated to 80 °C. After removal of the acetonitrile, the ¹H NMR spectrum of the residue revealed the presence of the cis,trans-diene **7** and a diastereomeric mixture of two siloxetanes (**8**) in a ratio of 74:13:13, respectively.

Compounds 7 and 8 were identified by comparison of the ¹H NMR spectral data with those reported in the literature.^{7a} The structures of 7 and 8 are only consistent with the initial formation of a 1,4-biradical intermediate, and therefore, the mechanism of addition of aldehydes to silene **3a** remains unchanged in a solvent of high dielectric constant. Also, the ratio of 7 to 8 in CH₃CN is similar to the ratio obtained in C₆D₆ (7:8:9 = 74:21:5).^{7a}

Although the ratio of 7 to 8 appears unaltered in CH_3CN , it is possible that heating the reaction mixture to dissolve the dimer influenced the final product ratio, particularly since siloxetanes are often thermally unstable. Therefore, the stability of compounds 7 and 8 at elevated temperatures was investigated. A CD_3CN solution containing cis,trans-diene 7 and two diastereomers of 8 was heated in an oil bath at 80 °C for 3 h. After heating, the mixture was analyzed by ¹H NMR spectroscopy; the ratio of compounds remained unaltered, and no evidence for the formation of new compounds was observed.

The addition of aldehyde 1 to neopentylsilene 4 in CH₃CN was also attempted. Neopentylsilene 4 was prepared in pentane, which was then removed under vacuum to give a yellow residue. A 0.3 M solution of 1 in CH₃CN was added to the residue, which did not dissolve. Although the ¹H NMR spectrum of the crude reaction mixture revealed the presence of 11 and small amounts of 12, two new compounds, 13 and 14, were found in significant quantities. The formation of both compounds was also observed in the addition of excess acetonitrile to a solution of silene 4 in benzene (Scheme 6). After isolation and purification by thin-layer chromatography, compound 13 was identified by ¹H, ¹³C, gCOSY, ¹H-¹³C gHSQC and gHMBC, and ¹H-²⁹Si gHMBC NMR spectroscopy, IR, and mass spectrometry as a CH insertion adduct between silene 4 and acetonitrile. Compound 14 was not isolated from the chromatographic plate, and hence, the structure of compound 14 was deduced on the basis of spectroscopic analysis (NMR and MS) of the crude product mixture. EI-MS revealed the presence of a 2:1 silene to acetonitrile adduct in addition to the 1:1 adduct. The presence of two different Mes₂SiCH₂CH₂-t-Bu moieties was apparent from the NMR data. Three signals in the NMR spectra of 14 were particularly diagnostic: a singlet at 2.68 ppm in the ¹H NMR spectrum of 14 which showed a one-bond coupling (~150 Hz) to the signal at 19.48 ppm (identified as a CH carbon by DEPT) and long-range coupling to the signal at 170.43 ppm (identified as a quaternary carbon) in the ¹³C dimension of the ${}^{1}H^{-13}C$ gHMBC spectrum of 14. The chemical shifts of these signals are in excellent agreement with the ¹H chemical shift of a related

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Scheme 7. Proposed Mechanism of the Addition Acetonitrile to Silene 4



keteniminic ¹H (3.33 ppm)¹³ and the predicted (HF) ¹³C chemical shifts of a silylated ketenimine (21.2 and 174.5 ppm, respectively).^{14,15} Together, the data support the structure of the disilylated ketenimine **14**. The presence of only two different mesityl substituents in the NMR spectra of **14** indicates that either the geometry at the nitrogen is linear in the ketenimine or it is undergoing rapid inversion at room temperature.¹⁶

The formation of ester 11 and vinylsilane 12 indicates, once again, that the outcome of the addition of aldehyde 1 to silene 4 in acetonitrile is similar to the reaction in pentane. Given that the yield of ester 11 is quite variable when the reaction is carried out in pentane, that the silene is quite insoluble in acetonitrile, and that the solvent, acetonitrile, competes with aldehyde 1 for reaction with the silene, it is difficult to interpret the difference in the product ratios.

Only a few nitrile adducts of silenes have been previously isolated.¹⁷ Sommer et al. reported the addition of acetonitrile, propionitrile, dimethylacetonitrile, and phenylacetonitrile to the transient Me₂Si=CH₂ (15).^{17b} As in the addition of CH₃CN to silene **4**, the α -CH bond of each nitrile adds across the double bond of silene **15**. We believe that the addition of CH₃CN to silene **4** begins with initial complexation of CH₃CN to the silenic silicon (Scheme 7).^{18,19} After complexation, presumably the former silenic carbon would

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(18) The formation of Lewis acid–base adducts with silenes is well-known,³ although not with acetonitrile.^{6b}

(19) The formation of nitrile/isonitrile adducts of disilynes has recently been described: (a) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2008**, *130*, 16848. (b) Takeuchi, K.; Ichinohe, M.; Sekiguchi, A.; Guo, J.-D.; Nagase, S. *Organometallics* **2009**, *28*, 2658. be more basic and, thus, could abstract the weakly acidic α -H from another molecule of CH₃CN. The anion generated by abstraction could then attack the silenic silicon, displacing the coordinated nitrile. Without initial coordination of acetonitrile to the silene, the silene itself would likely be too weak a base to react with acetonitrile. Compound **14** is a 2:1 adduct between the silene and acetonitrile.^{17c} The addition of silene **4** to **13** in benzene does indeed lead to the formation of adduct **14**, although the reaction is slow and the conversion is not clean. The adduct may be formed by coordination of the nitrile moiety of **13** to silene **4** followed by an ene reaction.

Given that kinetic studies of the related Ph₂Si=CH(CH₂-*t*-Bu) can be carried out in acetonitrile and that the transient UV absorption maxima of Ph₂Si=CH(CH₂-*t*-Bu) are the same in hexane and acetonitrile, ^{6b} we were initially surprised at the ease with which the reaction between Mes₂Si=CH-(CH₂-*t*-Bu) and acetonitrile takes place. However, in the previous study, the silene was found to be unchanged on the *microsecond* time scale in acetonitrile and product studies were not carried out, a sufficient variation in experimental protocols to account for the differences observed.

In summary, the addition of cyclopropyl aldehyde 1 to $Mes_2Si=SiMes_2(2)$, $(Me_3Si)_2Si=C(OSiMe_3)(t-Bu)$ (3a), and $Mes_2Si=CH(CH_2-t-Bu)$ (4) in acetonitrile was examined and the results were compared to the same reactions performed in hydrocarbon solvents. In all three cases, the change to a solvent of higher dielectric constant does not appear to be sufficient to change the nature of the reactive intermediate or to significantly change the ratio of the products.

During the course of this study, silene 4 was found to react with CH_3CN to give two adducts: compounds 13 and 14. Our results indicate that caution should be exercised when carrying out studies of transient silenes in acetonitrile as, clearly, the solvent may react with the substrate. The 1:1 adduct, compound 13, may find application in the preparation of more complex silicon-containing compounds, since the nitrile group may be further functionalized by simple chemical procedures. Surprisingly, the addition of nitriles to (di)metallenes has not been thoroughly examined, and thus, we continue to explore the generality of this potentially useful reaction.

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Supporting Information Available: Text giving general experimental details, experimental details of the addition of 1 to 2, 3a, and 4 and of acetonitrile to 4, and spectroscopic data of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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