

Preliminary communication

Silacyclopropanes from the reaction of silenes with Wittig reagents *

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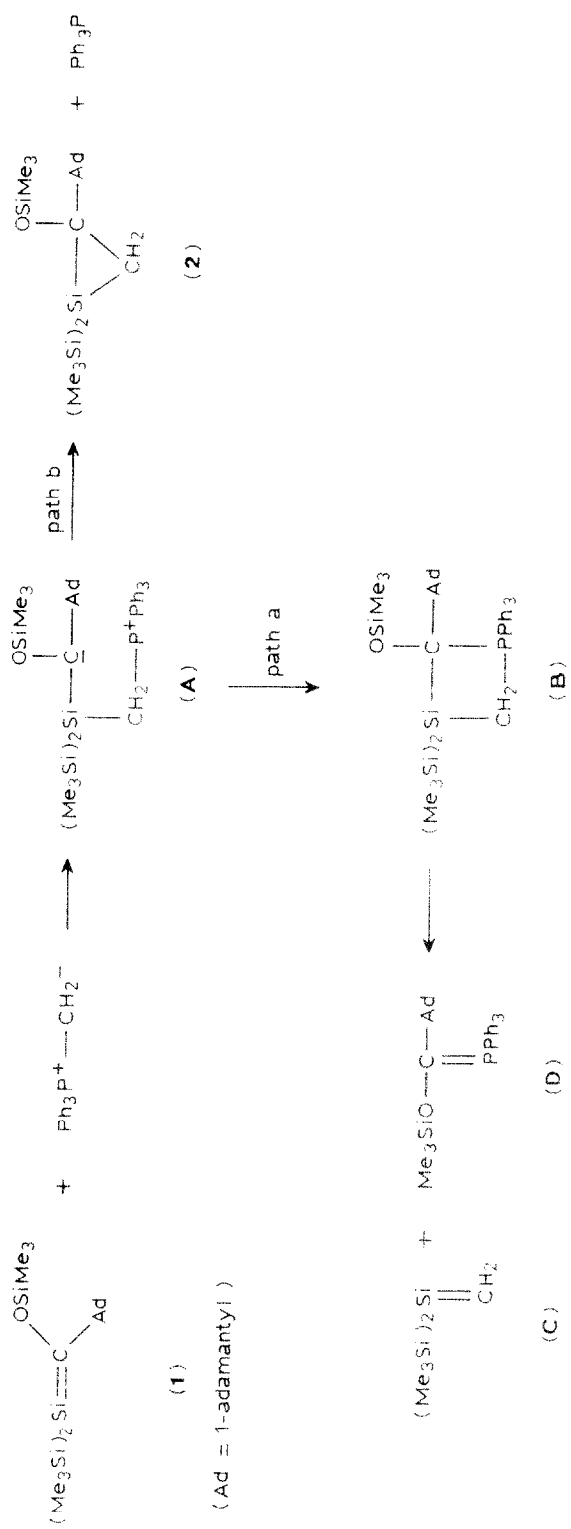
Abstract

The stable silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{Ad}$ (Ad = adamantyl) was found to react with the phosphorous ylid $\text{Ph}_3\text{P}^+\text{CH}_2^-$ or its sulfur analog to form the related silacyclopropane, as shown by NMR spectroscopy and by derivatization with methanol or acetophenone.

The similarity in bond polarization of a silicon–carbon double bond, $\text{Si}^{\delta+}=\text{C}^{\delta-}$, to that of a carbonyl group, $\text{C}^{\delta+}=\text{O}^{\delta-}$, suggests that reagents which react with the latter might also react with the former. Indeed, it is well established that alcohols add to both carbonyl compounds and silenes, and that other nucleophiles can add to silenes in the same sense that they add to carbonyl-containing compounds [1]. This led us to investigate the reaction of a stable silene $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{Ad}$ (Ad = adamantyl) with a simple Wittig reagent since our family of silenes $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)\text{R}$, while unusual in some of their behavior, clearly display typical $\text{Si}^{\delta+}=\text{C}^{\delta-}$ polarization in the sigma framework, as illustrated by their normal reactions with methanol [2], ketones [3], etc.

Two reaction pathways appear to be possible, either of which would be of interest. Assuming initial nucleophilic attack by the ylid at the silicon atom of the silene, the intermediary zwitterion **A** might behave like its carbonyl analog and form the silaphosphetane **B** (path a). In the event that **B** formed but was unstable, 2 + 2 retrocleavage would yield a new silene **C** and a new ylid **D**, both of which would be worthy of study. Alternatively **A** might react by intramolecular attack at the methylene carbon displacing triphenylphosphine, thus forming a silacyclopropane (silirane) **2** (path b). Related behavior has previously been observed in the reactions of a

* Dedicated to Professor Colin Eaborn, friend and colleague, and pioneer in the application of physical-organic methodology to organosilicon chemistry, for his many contributions to organometallic chemistry.



(1)

(A)

(2)

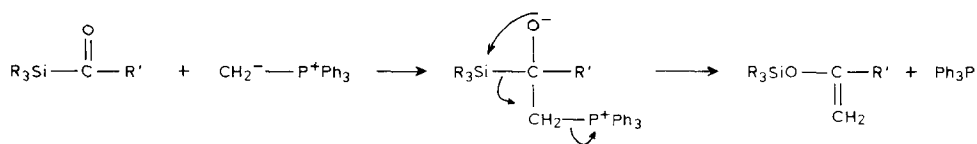
(Ad = 1-adamantyl)

(B)

(D)

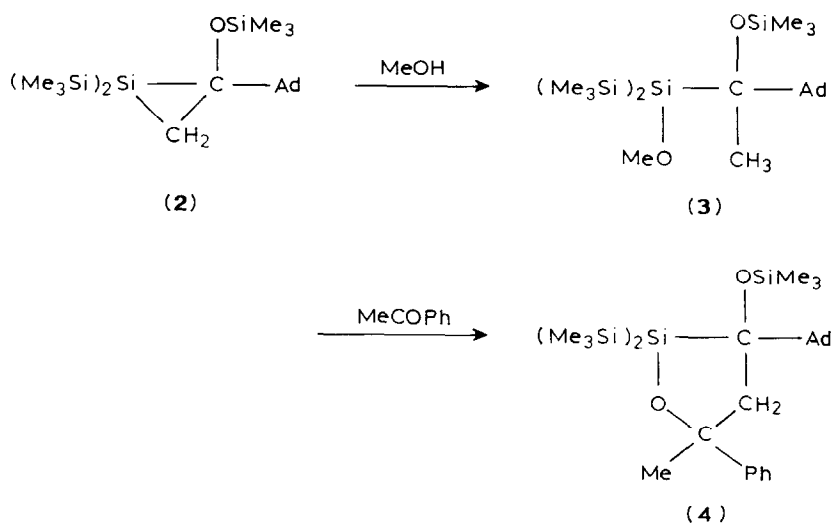
(C)

series of acylsilanes with phosphorus ylids in which the major products were silyl enol ethers and triphenylphosphine [4].



Treatment of the adamantylsilene **1**, derived by prior photolysis of 1-adamantanecarbonyltris(trimethylsilyl)silane [2], (1.0 g, 2.4 mmol) with methylene-triphenylphosphorane (prepared from 0.86 g (2.4 mmol) of methyltriphenylphosphonium bromide with 2.4 mmol of *n*-butyllithium in hexane/ C_6D_6) gave an immediate reaction, becoming initially a deep burgundy color which dissipated over 0.5 h to a yellow-brown color. After filtration under argon and dissolution in deuterobenzene, the ^{29}Si NMR spectrum of the crude reaction mixture indicated the presence of only one major product with a characteristic chemical shift at -47.9 ppm, typical of the ring silicon of a silacyclopropane such as **2**. The silicon atom of hexamethylsilirane resonates at -49.3 ppm [5] and other silacyclopropanes prepared by Seyferth had ^{29}Si NMR resonances in the range -51.8 to -53.2 ppm [6]. This strongly suggested the reaction had occurred via path b. **2**. NMR (C_6D_6): $\delta(^1\text{H})$ 0.52 (br m, 27H Me_3Si), 1.8–2.2 (br m, 17H, Ad + CH_2), 7.2 (Ph_3P) ppm; $\delta(^{29}\text{Si})$ -17.99 , -9.82 (Me_3Si), 10.54 (Me_3SiO), -47.93 (ring Si) ppm.

Confirmation of the formation of **2** was obtained by treatment of the same quantity of the reaction product with methanol, which gave an exothermic reaction, and the formation of a product assigned the structure of the expected methanol adduct **3**, based on ^1H , ^{13}C and ^{29}Si NMR data. **3**. NMR (CDCl_3): $\delta(^1\text{H})$ 0.17, 0.25, 0.27 (s, each 9H, Me_3Si), 1.57–2.17 (m, 15H, Ad), 2.03 (s, 3H, Me), 3.50 (s, 3H, MeO) ppm; $\delta(^{13}\text{C})$ 0.63, 0.65, 1.12 (Me_3Si), 28.65 (Ad-CH), 37.11, 40.85 (Ad- CH_2),



37.41 (Ad-quat-C), 29.70 (Me), 53.78 (MeO), 80.39 (quat-C-O) ppm; $\delta(^{29}\text{Si})$ – 17.37, – 19.10 (Me_3Si), 15.03 (Me_3SiO), 10.59 ($(\text{Me}_3\text{Si})_2\text{Si}$) ppm. These data were very similar to that of the methanol adduct of the original silene [7].

Further confirmation of the identity of the reaction product was obtained from its reaction with added acetophenone to yield the typical two-atom insertion product **4**. Seyferth has reported several examples of carbonyl insertions into the silirane ring [8]. Two diastereomers would be expected from reaction of **2** with acetophenone: the NMR data, which was entirely consistent with the proposed structure, indicated that one diastereomer was present in large (> 80%) excess. **4**. NMR (CDCl_3): $\delta(^{13}\text{C})$ – 0.88, – 0.34, 1.02 (Me_3Si), 27.01 (Me), 39.67 (CH_2 ?), 28.58 (Ad-CH), 37.10, 40.92 (Ad- CH_2), 37.20 (Ad-quat-C), 81.81, 104.23 (ring quat-C) ppm; $\delta(^{29}\text{Si})$ – 17.66, – 18.06 (Me_3Si), 6.58 (Me_3SiO), 16.40 (ring Si) ppm.

The reaction of the silene with the sulphur ylid dimethylsulphonium methylide gave essentially identical results as indicated by NMR spectroscopy, but the experimental manipulations were more difficult. Dimethylsulphonium methylide is not stable at room temperature, and the ylid must be made and used at low temperature (< 0°C). While this can be done readily using sodium methylsulfinylmethide as the base in dimethylsulphoxide/THF mixed solvent, DMSO could not be employed in the present study because of its potential reaction with the silene (currently under study in this laboratory). This led to the use of dichloromethylithium (generated from LDA in CH_2Cl_2 at low temperature) as the base to generate the ylid, but the low temperature and solubility problems made this a less desirable route to the silirane.

The generality of this route to siliranes is currently being explored in our laboratory.

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