

SILICON–CARBON MULTIPLE-BONDED ($p_{\pi}-p_{\pi}$) INTERMEDIATES

III*. REACTIONS OF THIOBENZOPHENONE WITH THERMALLY GENERATED 1,1-DISUBSTITUTED 1-SILAETHENES, $[R_2Si=CH_2]$: EVIDENCE FOR A $p_{\pi}-p_{\pi}$ SILICON–SULFUR DOUBLE-BONDED SPECIES

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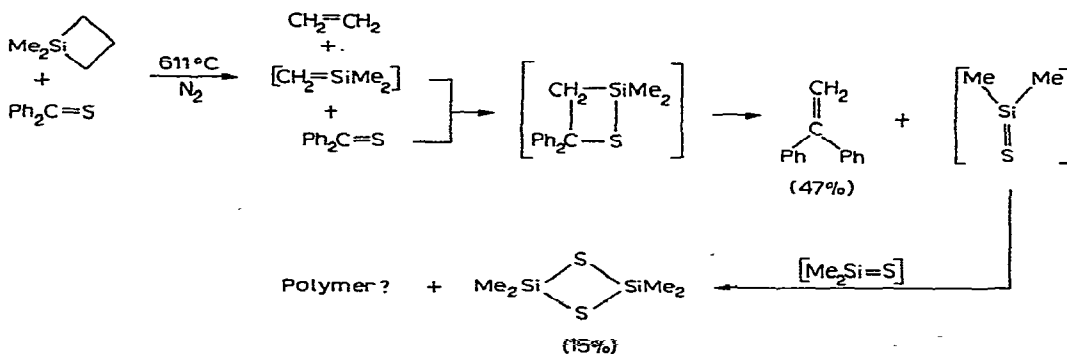
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Summary

Reactions of $[R_2Si=CH_2]$ ($R = Me, Ph$), generated by thermolysis of the corresponding 1,1-disubstituted silacyclobutane at $611^\circ C$, with $Ph_2C=S$ are described. A Wittig-like reaction takes place, yielding $Ph_2C=CH_2$ and what are believed to be the first examples of transient $[R_2Si=S]$.

It has previously been shown that when the reactive intermediate $[R_2Si=CH_2]$ (formed by vapor phase thermolysis of the corresponding 1,1-disubstituted silacyclobutane) is generated in the presence of a nonenolizable ketone such as benzophenone $Ph_2C=O$, a Wittig-like reaction takes place giving $Ph_2C=CH_2$ and transient monomeric $[R_2Si=O]$ [1]. In exploring the scope of this reaction we wondered whether $[R_2Si=CH_2]$ would react in a like manner with thiobenzo-

SCHEME 1



* For part II, see ref. 3.

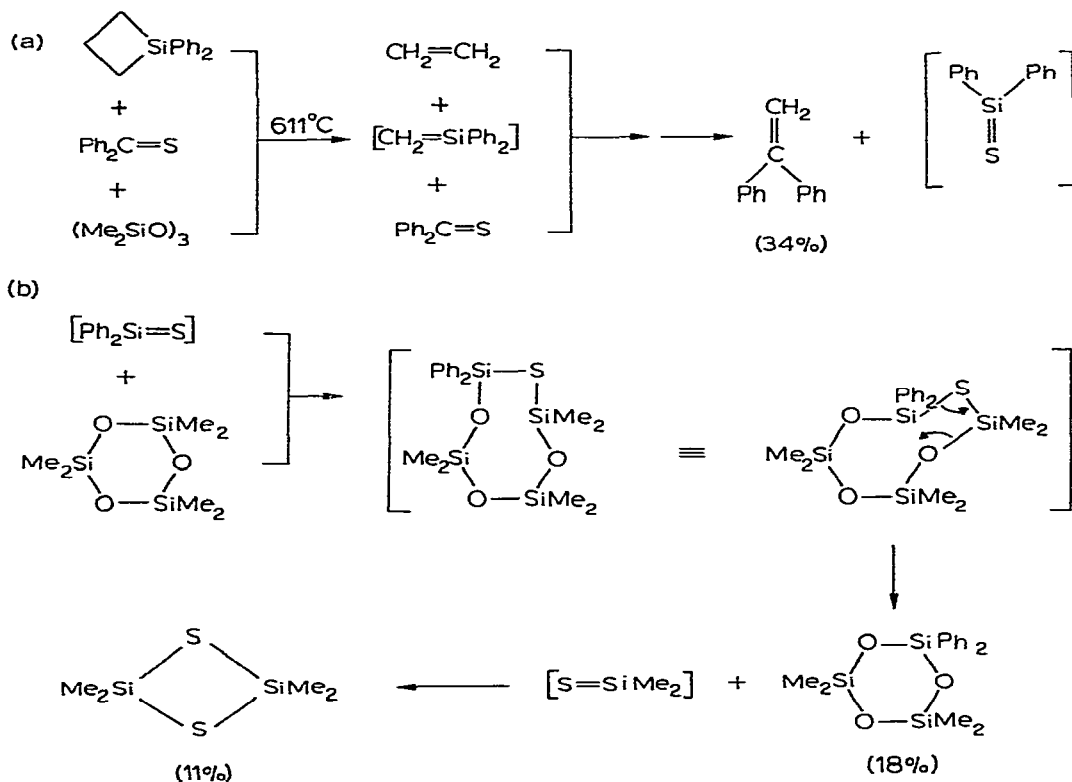
phenone $\text{Ph}_2\text{C}=\text{S}^*$ and give $[\text{R}_2\text{Si}=\text{S}]$. We report here evidence that this is indeed the case.

Scheme 1 indicates the reactants and products of an initial experiment and includes the mechanism we believe accounts for the transformation.

Specifically a benzene solution of 1,1-dimethylsilacyclobutane (5.0 mmol) and thiobenzophenone (3.4 mmol) was pyrolyzed at 611°C using the general procedure and equipment described earlier for generation of $[\text{Me}_2\text{Si}=\text{O}]$ [1]. The products were isolated from the reaction mixture by preparative GLC. 1,1-Diphenylethylene (47% yield) was identified by its IR and NMR spectra, and the silicon-sulfur product, tetramethylcyclodisilthiane (Me_2SiS)₂, (15% yield) was identified by its melting point and NMR spectrum. Minor products, detected by analytical GLC, were not identified.

As previously reported [1], formation of $[\text{Me}_2\text{Si}=\text{O}]$ in the vapor phase leads mainly to stable derivatives of itself in the form of the cyclic trimer $(\text{Me}_2\text{SiO})_3$ and tetramer $(\text{Me}_2\text{SiO})_4$, the dimer evidently being unstable, indeed an unknown compound. By contrast $[\text{Me}_2\text{Si}=\text{S}]$ readily forms its cyclic dimer $(\text{Me}_2\text{SiS})_2$, a crystalline compound [3]. It should be noted that the corresponding trimer $(\text{Me}_2\text{SiS})_3$ is converted to the dimer at temperatures above 200°C [3]. In our experiments we isolated only the dimer, although small amounts of the trimer may have been present.

SCHEME 2



* Thiobenzophenone is known to react analogously to benzophenone in the Wittig reaction [2].

We also thermolyzed 1,1-diphenylsilacyclobutane in the presence of thiobenzophenone, predicting the formation of transient $[\text{Ph}_2\text{Si}=\text{S}]$ and its dimerization to give $(\text{Ph}_2\text{SiS})_2$. However we did not detect this product in the reaction mixture, using analytical GLC and independently synthesized [4] $(\text{Ph}_2\text{SiS})_2$ as a reference standard. Unfortunately, the trimer, $(\text{Ph}_2\text{SiS})_3$, is not sufficiently volatile to allow analysis by analytical GLC. Attempts to crystallize $(\text{Ph}_2\text{SiS})_3$ from the reaction mixture were also unsuccessful. Firm indication that transient $[\text{Ph}_2\text{Si}=\text{S}]$ was formed, however, was given by the fact the expected olefinic co-product, i.e. 1,1-diphenylethylene, was obtained in 25% yield.

While due to difficulties in product analysis the fate of our predicted $[\text{Ph}_2\text{Si}=\text{S}]$ intermediate in the above reaction remains unknown, we are able to demonstrate its existence from the results of an additional experiment, in which a trapping agent for $[\text{Ph}_2\text{Si}=\text{S}]$ was added to the reaction mixture prior to thermolysis. The trapping agent, cyclic $(\text{Me}_2\text{SiO})_3$ has previously been shown [5] to trap $[\text{Me}_2\text{Si}=\text{O}]$ by insertion into the ring, to give ring expansion by one Si-O unit. Thus we expected analogous ring expansion by insertion of one Si-S unit. This appears to be the case, except that the ring-expanded species is unstable with respect to two other species, the observed products which are shown in Scheme 2.

The products, $[\text{Me}_2\text{Si}=\text{S}]$ dimer (11% yield) and 1,1,3,3-tetramethyl-5,5-diphenylcyclotrisiloxane (18% yield), can be readily explained by extrusion of $[\text{Me}_2\text{Si}=\text{S}]$ from the ring expanded species.

In our view these initial experiments clearly implicate $[\text{R}_2\text{Si}=\text{S}]$ as a reactive intermediate quite analogous to $[\text{R}_2\text{Si}=\text{O}]$, $[\text{R}_2\text{Si}=\text{CH}_2]$, and $[\text{R}_2\text{Si}=\text{NR}']$ [6]. While their bonding nature needs yet to be elucidated exactly, these species continue to unfold interesting chemistry.

Experimental

Thermolysis of 1,1-dimethylsilacyclobutane in the presence of thiobenzophenone

This thermolysis, as well as the others reported below, was carried out at 611°C in a stream of nitrogen (flow rate 25 ml/min) within a quartz tube heated in a 750 Watt furnace. The thermolysate was collected in a cold trap at 0°C. A detailed description of the apparatus and general procedure has been published previously [1].

A solution consisting of 0.500 g (5.0 mmol) of 1,1-dimethylsilacyclobutane [1], 0.674 (3.4 mmol) of thiobenzophenone [7] and 2.0 ml of benzene was thermolyzed with an addition time of 7.6 min. An additional 2.0 ml of benzene was slowly passed through the heated tube as a wash, combining in the cold trap with the original pyrolysis fraction to give 4.0 ml of product solution colored blue by a small amount of unreacted thiobenzophenone.

Resolution of the product mixture by preparative GLC (general method described previously [1]) gave 0.046 g (15% yield) of crystalline tetramethylcyclodisilthiane $(\text{Me}_2\text{SiS})_2$, identified by its m.p. (109-111°C, lit. [3] 108-110°C) and NMR spectrum [8] (Si-CH₃ singlet at δ 0.72 ppm), and 0.288 g (47% yield) of 1,1-diphenylethylene identified by comparison of its IR and NMR spectra

with those of authentic material. Minor components of the reaction mixture, including unreacted thiobenzophenone, were not collected.

Thermolysis of 1,1-diphenylsilacyclobutane in the presence of thiobenzophenone

A solution consisting of 0.557 g (2.5 mmol) of 1,1-diphenylsilacyclobutane [1], 0.337 g (1.7 mmol) of thiobenzophenone, and 2.0 ml of benzene was thermolyzed with an addition time of 9.2 min. An additional 2.0 ml of benzene was then passed through the thermolysis tube, giving a total of 4.2 ml of blue-green solution in the cold trap.

GLC analysis of the solution showed the presence of 1,1-diphenylethylene plus a number of minor components. However no chromatogram peak corresponding to the expected silicon-sulfur product, $(\text{Ph}_2\text{SiS})_2$, was observed. The retention time of this compound in the chromatogram was ascertained by the addition of authentic $(\text{Ph}_2\text{SiS})_2$, independently synthesized [4], to a sample of the product mixture. It was further found that the corresponding trimer $(\text{Ph}_2\text{SiS})_3$, also independently synthesized [4], is insufficiently volatile to show a peak in the chromatograph, even at column temperatures of 260°C . Thus if $(\text{Ph}_2\text{SiS})_3$ is formed in the above thermolysis, we could not detect it by our GLC analysis. Attempts to crystallize this possible product (m.p. 186° , ref. 4) from the product mixture met with failure. Preparative GLC gave 0.077 g (25% yield) of 1,1-diphenylethylene, identified by its IR spectrum.

Thermolysis of 1,1-diphenylsilacyclobutane in the presence of thiobenzophenone and trapping agent $(\text{Me}_2\text{SiO})_3$

A solution consisting of 0.557 g (2.5 mmol) of 1,1-diphenylsilacyclobutane, 0.337 g (1.7 mmol) of thiobenzophenone, 0.754 g (3.4 mmol) of hexamethylcyclotrisiloxane, and 2.0 ml of benzene was thermolyzed with an addition time of 10.1 min. An additional 2.0 ml of benzene was passed through the thermolysis tube, giving a total of 4.8 ml of blue-green solution in the cold trap.

Resolution of the product mixture gave 0.0157 g (11% yield) of crystalline tetramethylcyclodisilthiane, m.p. $109\text{--}111^\circ\text{C}$ (lit. [3] $108\text{--}110^\circ\text{C}$), 0.1056 g (34% yield) of 1,1-diphenylethylene identified by its IR spectrum, and 0.1069 g (18% yield) of 1,1,3,3-tetramethyl-5,5-diphenylcyclotrisiloxane identified by its IR, NMR and mass spectra. Mass spectrum major peaks m/e (rel. int.) 346(46), 331(100), 315(9.7), 269(23), 253(82). Exact mass measurement on the 346 peak, found: 346.0891. $\text{C}_{16}\text{H}_{22}\text{O}_3\text{Si}_3$ calcd.: 346.0877. NMR (CCl_4) δ 0.12 Si- CH_3 singlet plus aromatic protons. IR (CCl_4) 1430s (Si-Ph), 1260s (Si- CH_3), 1120s, 1130s (Si-Ph), 1050s cm^{-1} (Si-O-Si)*.

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* One of the referees suggested that formation of the observed products might follow a mechanistic pathway other than that given in Scheme 2. His suggestion, that 1,1-diphenyl-1-silaethene inserts into $(\text{Me}_2\text{SiO})_3$ followed by splitting out of 1,1-dimethyl-1-silaethene which then gives tetramethylcyclodisilthiane, was shown to be incorrect by a control experiment utilizing 1,1-diphenyl-1-silacyclobutane and $(\text{Me}_2\text{SiO})_3$. These gave the 1/1 adduct from the insertion of $\text{Ph}_2\text{Si}=\text{CH}_2$ into the Si-O bond of $(\text{Me}_2\text{SiO})_3$ as a stable isolable compound, and none of the 1,1,3,3-tetramethyl-5,5-diphenylcyclotrisiloxane, expected on the basis of the referee's hypothesis.

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