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SILICON—CARBON MULTIPLE-BONDED (p_π—p_π) INTERMEDIATES

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

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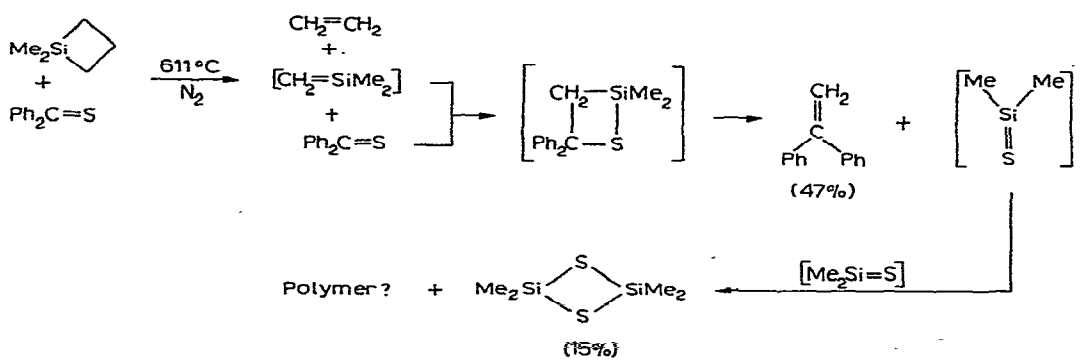
Summary

Reactions of [$R_2Si{=}CH_2$] (R = Me, Ph), generated by thermolysis of the corresponding 1,1-disubstituted silacyclobutane at 611°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. 9.

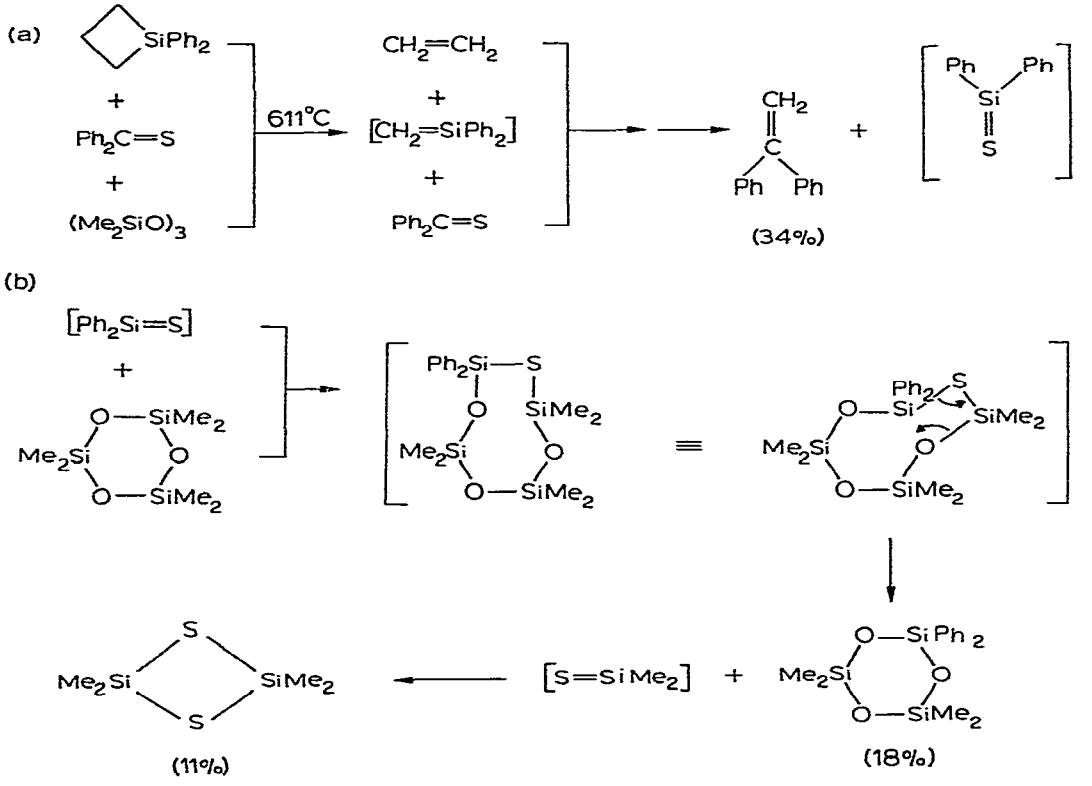
phenone $Ph_2C{=}S$* and give $[R_2Si{=}S]$. We report here evidence that this is indeed the case.

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 $[Me_2Si{=}O]$ [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 $[Me_2Si{=}O]$ in the vapor phase leads mainly to stable derivatives of itself in the form of the cyclic trimer $(Me_2SiO)_3$ and tetramer $(Me_2SiO)_4$, the dimer evidently being unstable, indeed an unknown compound. By contrast $[Me_2Si{=}S]$ readily forms its cyclic dimer $(Me_2SiS)_2$, a crystalline compound [3]. It should be noted that the corresponding trimer $(Me_2SiS)_3$ 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 [$Ph_2Si{=}S$] and its dimerization to give $(Ph_2SiS)_2$. However we did not detect this product in the reaction mixture, using analytical GLC and independently synthesized [4] $(Ph_2SiS)_2$ as a reference standard. Unfortunately, the trimer, $(Ph_2SiS)_3$, is not sufficiently volatile to allow analysis by analytical GLC. Attempts to crystallize $(Ph_2SiS)_3$ from the reaction mixture were also unsuccessful. Firm indication that transient [$Ph_2Si{=}S$] was formed, however, was given by the fact the expected olefinic coproduct, i.e. 1,1-diphenylethylene, was obtained in 25% yield.

While due to difficulties in product analysis the fate of our predicted [$Ph_2Si{=}S$] 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 [$Ph_2Si{=}S$] was added to the reaction mixture prior to thermolysis. The trapping agent, cyclic $(Me_2SiO)_3$ has previously been shown [5] to trap [$Me_2Si{=}O$] 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, [$Me_2Si{=}S$] dimer (11% yield) and 1,1,3,3-tetramethyl-5,5-diphenylcyclotrisiloxane (18% yield), can be readily explained by extrusion of [$Me_2Si{=}S$] from the ring expanded species.

In our view these initial experiments clearly implicate [$R_2Si{=}S$] as a reactive intermediate quite analogous to [$R_2Si{=}O$], [$R_2Si{=}CH_2$], and [$R_2Si{=}NR'$] [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 $(Me_2SiS)_2$, identified by its m.p. (109-111°C, lit. [3] 108-110°C) and NMR spectrum [8] (Si—CH_3 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, $(Ph_2SiS)_2$, was observed. The retention time of this compound in the chromatogram was ascertained by the addition of authentic $(Ph_2SiS)_2$, independently synthesized [4], to a sample of the product mixture. It was further found that the corresponding trimer $(Ph_2SiS)_3$, also independently synthesized [4], is insufficiently volatile to show a peak in the chromatograph, even at column temperatures of 260°C. Thus if $(Ph_2SiS)_3$ 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 $(Me_2SiO)_3$

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. 109-111°C (lit. [3] 108-110°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. $C_{16}H_{22}O_3Si_3$ 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 $(Me_2SiO)_3$ 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 $(Me_2SiO)_3$. These gave the 1/1 adduct from the insertion of $Ph_2Si{=}CH_2$ into the Si—O bond of $(Me_2SiO)_3$ 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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