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Preliminary communication

A NEW ROUTE TO DIMETHYLSILANONE [$(CH_3)_2Si{=}O$]; DEOXYGENATION OF DIMETHYLSULFOXIDE BY DIMETHYLSILYLENE

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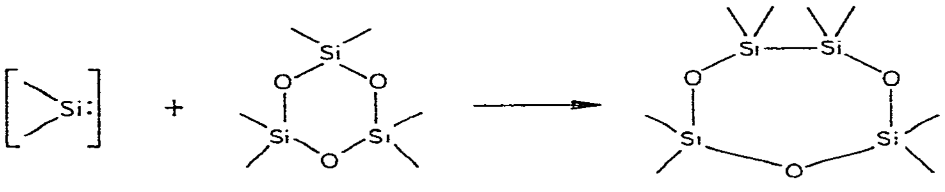
Summary

Dimethylsilylene has been shown to insert in Si—O single bonds of hexamethylcyclotrisiloxane to yield 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane. Dimethylsilylene has also been shown to deoxygenate dimethyl sulfoxide to yield dimethyl sulfide and dimethylsilanone which can be trapped.

Photolysis of dodecamethylcyclohexasilane (I) (λ_{max} 2520 Å, ϵ 1200) [1] has been shown to yield dimethylsilylene (II) [2]. We should like to report two new reactions of II. Thus photolysis of a dioxane solution of I in the presence of a two-fold molar excess of hexamethylcyclotrisiloxane (III) yields 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane (IV) [3] in 52% yield based on the number of moles of I. Formation of this product probably results from insertion of II into the Si—O single bond of III. It should be noted that both III and IV possess only end absorption (below 2200 Å) in the ultraviolet. While this is the first report of insertion of a silylene into the Si—O single bond of a siloxane, insertion of II into Si—O single bonds of dimethoxydimethylsilane has been previously observed [2, 4]. By comparison, control experiments showed that dimethylsilylene does not insert into the C—O single bond of dioxane.



(II) (III) (IV)

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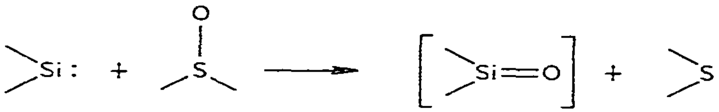
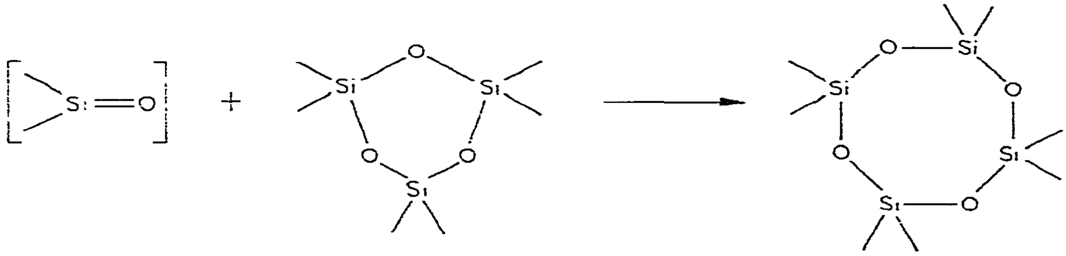
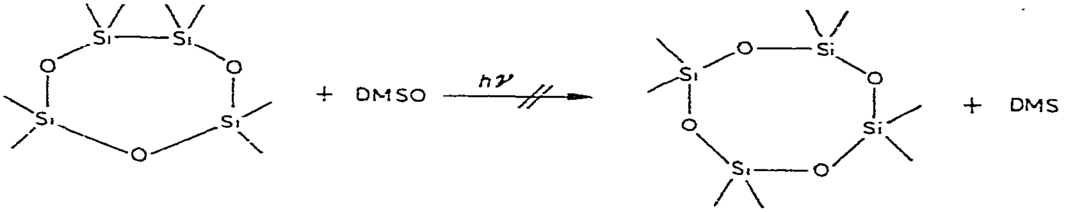
On the other hand, photolysis of a dioxane solution of I in the presence of a two-fold molar excess of dimethyl sulfoxide (DMSO) leads to an almost quantitative yield of dimethyl sulfide (DMS). This result can be explained if II is capable of deoxygenating DMSO to yield DMS and a reactive intermediate possessing a silicon—oxygen double bond (dimethylsilanone). The analogous reaction in which carbenes deoxygenate DMSO to yield DMS is known [5].



Further, photolysis of a dioxane solution of I in the presence of a two-fold molar excess of DMSO and III leads to formation of DMS (≃ 90%), IV (12%), and octamethylcyclotetrasiloxane (V) (44%, based on the number of moles of I). These experimental results are consistent with the intermediacy of dimethylsilanone which is trapped by insertion of its Si—O double bond into the Si—O single bond of III to yield V. Analogous insertion reactions have been reported. High temperature pyrolysis of V leads to the microscopic reverse of this insertion reaction [6, 7]. In addition, reactive intermediates possessing Si—O double bonds, generated by Wittig-like reactions of Si—C double bonded intermediates with non-enolizable ketones such as benzophenone [8—10], have been shown to insert their Si—O double bonds into Si—O single bonds [11, 12].



An alternative interpretation, namely that IV reacts with DMSO to yield DMS and V, was ruled out by control experiments. Thus IV was shown to be stable to DMSO in the presence and absence of light. Such control experiments were neces-



sary since Si—Si single bonds are known to be oxidized to Si—O—Si bonds by perbenzoic acid [13].

Thus, we conclude that II can deoxygenate DMSO to yield dimethylsilanone and DMS. Tertiary amine oxides are also deoxygenated by II to yield tertiary amines [14]. Similar results [14] have been obtained with methylphenylsilylene [15].

Experimental

Photolysis of I in the presence of III

A solution of 0.174 g (0.5 mmol) of I, 0.22 g (1.0 mmol) of III, and 3.54 g (40 mmol) of purified dioxane were placed in a quartz NMR tube. Oxygen was removed by bubbling purified N_2 through the solution for 15 min prior to photolysis. This mixture was photolyzed at 25°C for 1.5 h using a 450 Watt medium pressure Hanovia Hg lamp. The solution was subjected to bulb-to-bulb distillation under reduced pressure (20 mmHg). The distillate was analyzed by preparative GLPC on a 1/4″ × 18″ 20% SE-30 chromosorb P column at 90°C. In this manner, 0.073 g (0.26 mmol) of IV (52% yield, based on the number of moles of I) was obtained. Spectral properties of IV were consistent with those reported [3]. IR: 1050 cm^{-1} Si—O; NMR: δ 0.07 (s, 12H), and 0.2 ppm (s, 12H). In addition 0.16 g (0.72 mol) of III was recovered.

Photolysis of I

A solution of 0.174 g (0.5 mmol) of I and 3.54 g (40 mmol) of purified dioxane were placed in a quartz NMR tube. Oxygen was removed as above. Photolysis of this solution resulted in a mixture of silicon containing products similar to those observed on photolysis of I in cyclohexane [2]. No products resulting from reaction of dimethylsilylene with dioxane were observed.

Photolysis of I in the presence of DMSO

DMSO (0.078 g, 1.0 mmol) was added to a solution whose composition was identical to that reported above. Photolysis of this solution under similar conditions led to an almost quantitative yield of dimethyl sulfide.

Photolysis of I in the presence of DMSO and III

A solution composed of 0.174 g (0.5 mmol) of I, 0.078 g (1.0 mmol) of DMSO, 0.222 g (1.0 mmol) of III, and 3.52 g (40 mmol) of dioxane was irradiated as above. Analysis of the volatile products indicated DMS ($\simeq$ 90%), IV (0.016 g, 0.057 mmol, 11.4%) and V (0.066 g, 0.22 mmol, 44%; yields based on the number of moles of I) as well as 0.16 g (0.72 mmol) of recovered III.

Photolysis of IV with DMSO

A mixture composed of 0.031 g (0.11 mmol) of IV, 0.0345 g (0.44 mmol) of DMSO and 1.55 g (17.7 mmol) of dioxane was photolyzed under the same conditions as the above reactions. GLPC analysis of the resulting solution indicated neither any degradation of IV nor any formation of V.

This mixture was allowed to stand for 24 h at 25°C in the absence of light. Analysis by GLPC again indicated no change in IV.

Acknowledgement

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