

THE OXIDATION OF SILANES IN
DIMETHYL SULFOXIDE

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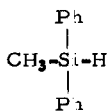
(Received 15 June 1964; in revised form 5 October 1964)

In the course of studying the behavior of silanes in the presence of strong bases, we have found that di- and trisubstituted silanes react with the conjugate base of dimethyl sulfoxide* to yield oxygenated silicon compounds. The reaction is extremely rapid and quantitative. Dimethyl sulfide is evolved as the reduced product. Both the type of silicon containing compounds and the amount of dimethyl sulfide are functions of the relative concentrations of the dimethyl sulfoxide anion and the silane.

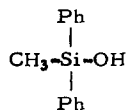
Methyldiphenylsilane (I), when added to a solution of dimethyl sulfoxide containing one equivalent of dimethyl sulfoxide anion, reacts at room temperature, and dimethyl sulfide is evolved. The reaction mixture was worked up 10 minutes after the addition of the silane. Dilute aqueous hydrochloric acid was added and the organic materials extracted with ether. An infra red spectrum of the product mixture indicated that the starting material had reacted completely as the 4.7μ Si-H stretching frequency was absent. The absence of the quartet at 5.0τ of the starting material confirmed the above observation. The

* The conjugate base of dimethyl sulfoxide was produced utilizing sodium hydride. The required quantity of a 56% sodium hydride-mineral oil dispersion was washed three times with pentane to remove the mineral oil. The final traces of pentane were removed by a stream of nitrogen. Freshly distilled dimethyl sulfoxide was added to the sodium hydride. After heating at 60° for one half hour, the clear solution was cooled to room temperature and used immediately. All reactions were carried out under a nitrogen atmosphere.

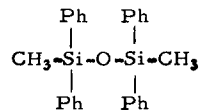
reaction product consisted of a mixture of methyldiphenylsilanol (II) and bis-(methyldiphenyl)-siloxane (III) in the ratio of 4.3 to 1. Analysis was performed utilizing the intensities of the methyl singlets (n. m. r.) of each compound.



I



II



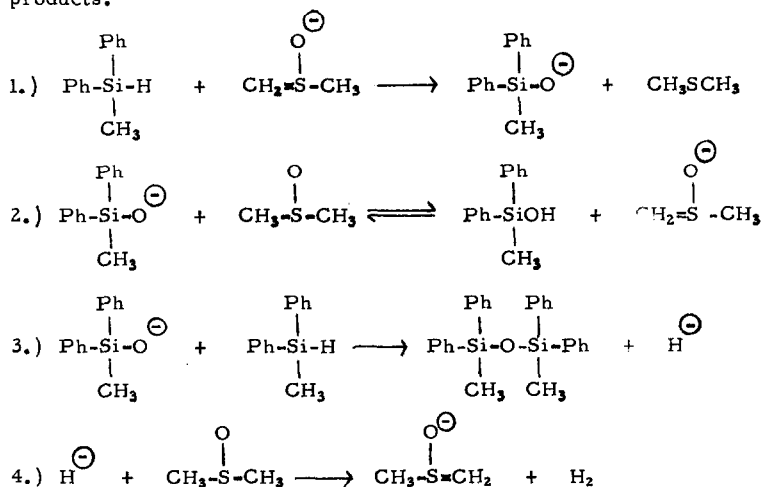
III

That the oxygenated products are not derived from the aqueous work up was confirmed by utilizing anhydrous hydrogen bromide for neutralization. Vacuum transfer of dimethyl sulfoxide and dissolution of silicon containing compounds from the resultant residue in ether yielded the identical products that were observed in the aqueous work up.

The product ratio is a function of the relative amounts of dimethyl sulfoxide anion and silane. When a two-fold excess of the anion of dimethyl sulfoxide was employed, only the silanol was obtained. When one tenth of an equivalent of the dimethyl sulfoxide anion was used, the sole product was the siloxane. The silane was completely consumed in the latter case indicating that only a catalytic quantity of base is required for the reaction.

Methyldiphenylsilane is stable to dimethyl sulfoxide in the absence of the dimethyl sulfoxide anion. It is therefore likely that the attacking species is the anion of dimethyl sulfoxide which transfers oxygen to the silicon atom. However the dimethyl sulfoxide anion must be regenerated in order to allow the reaction to occur quantitatively when the concentration of the anion is less than stoichiometric. The relative yields of silanol and

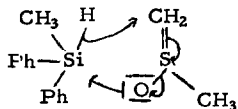
siloxane can be rationalized as the siloxane undoubtedly results from attack of the anion of the silanol on unreacted silane when the base concentration is sufficiently low to allow competition to occur. The following reaction sequence is proposed to explain the observed products.



In order to provide supporting evidence for the proposed oxidation pathway the following additional experiments were carried out. Addition of a tenth of an equivalent of the sodium salt of methyldiphenylsilanol to dimethyl sulfoxide produced a solution that oxidized methyldiphenylsilane with the same facility as a solution containing the anion of dimethyl sulfoxide. The yield of dimethyl sulfide was determined by sweeping the system with nitrogen and trapping condensable material at -78° . The contents of the trap were warmed to 50° and the yield of dimethyl sulfide determined manometrically. In two experiments utilizing three

equivalents of the conjugate base of dimethyl sulfoxide, 0.81 and 0.89 equivalents of dimethyl sulfide were obtained. Utilizing catalytic quantities of the conjugate base of dimethyl sulfoxide 0.42 and 0.47 equivalents of dimethyl sulfide were produced in two trials. The observed quantities of dimethyl sulfide are in agreement with those predicted by the proposed oxidative scheme. At high base concentrations one equivalent of dimethyl sulfide is predicted whereas with catalytic quantities of base one half equivalent of dimethyl sulfide should be produced.

The exact mechanism by which the oxidation step occurs has not been established. However, a reasonable cyclic mechanism, in which simultaneous transfer of oxygen and hydrogen occurs, can be written.



Diphenylsilane also undergoes the oxidation reaction under conditions where an equivalent of base is employed. Octaphenylcyclotetrasiloxane is produced and dimethyl sulfide is evolved.