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MERCURY-SENSITIZED PHOTOLYSIS OF PENTAMETHYLDISILANE AND *sym*-TETRAMETHYLDISILANE

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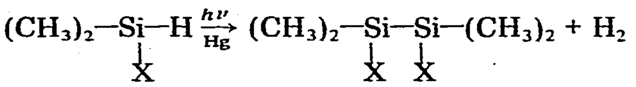
Summary

Photolysis of pentamethyldisilane in the vapor phase in the presence of mercury yields decamethyltetrasilane and octamethyltrisilane as major products. Photolysis of *sym*-tetramethyldisilane yields 1,3-dihydrohexamethyltrisilane and 1,4-dihydrooctamethyltetrasilane. The mechanism of formation of these products is discussed.

There are few Si—Si bond forming reactions [1,2]. For this reason, we have been concerned with the scope and limitations of the vapor phase photolysis of silanes in the presence of mercury which was shown some ten years ago to yield disilanes. Among the examples initially reported by Gunning et al. were the photolysis of trimethylsilane to yield hexamethyldisilane and the photolysis of dimethylsilane to yield *sym*-tetramethyldisilane ($H—Si_2—H$) [3]. Subsequently, Urry et al. showed that photolysis of chlorodimethylsilane yields 1,2-dichlorotetramethyldisilane [4]. Recently, we reported that photolysis of dimethoxymethylsilane yields *sym*-tetramethoxydimethyldisilane [5]. Apparently, this photochemical Si—Si bond forming reaction is applicable to the synthesis of disilanes possessing $Si—CH_3$, Si—H, Si—Cl, and $Si—OCH_3$ bonds.



$$(CH_3)_2—\underset{\underset{X}{|}}{Si}—H \xrightarrow[Hg]{h\nu} (CH_3)_2—\underset{\underset{X}{|}}{Si}—\underset{\underset{X}{|}}{Si}—(CH_3)_2 + H_2$$

($X = CH_3$, H, Cl, OCH_3)

We should like to report that this reaction is also applicable to the synthesis of tri- and tetra-silanes by photolysis of the appropriate disilanes possessing at least one Si—H bond. Thus photolysis of pentamethyldisilane ($CH_3—Si_2—H$) [6] in the vapor phase in the presence of mercury yields decamethyltetrasilane

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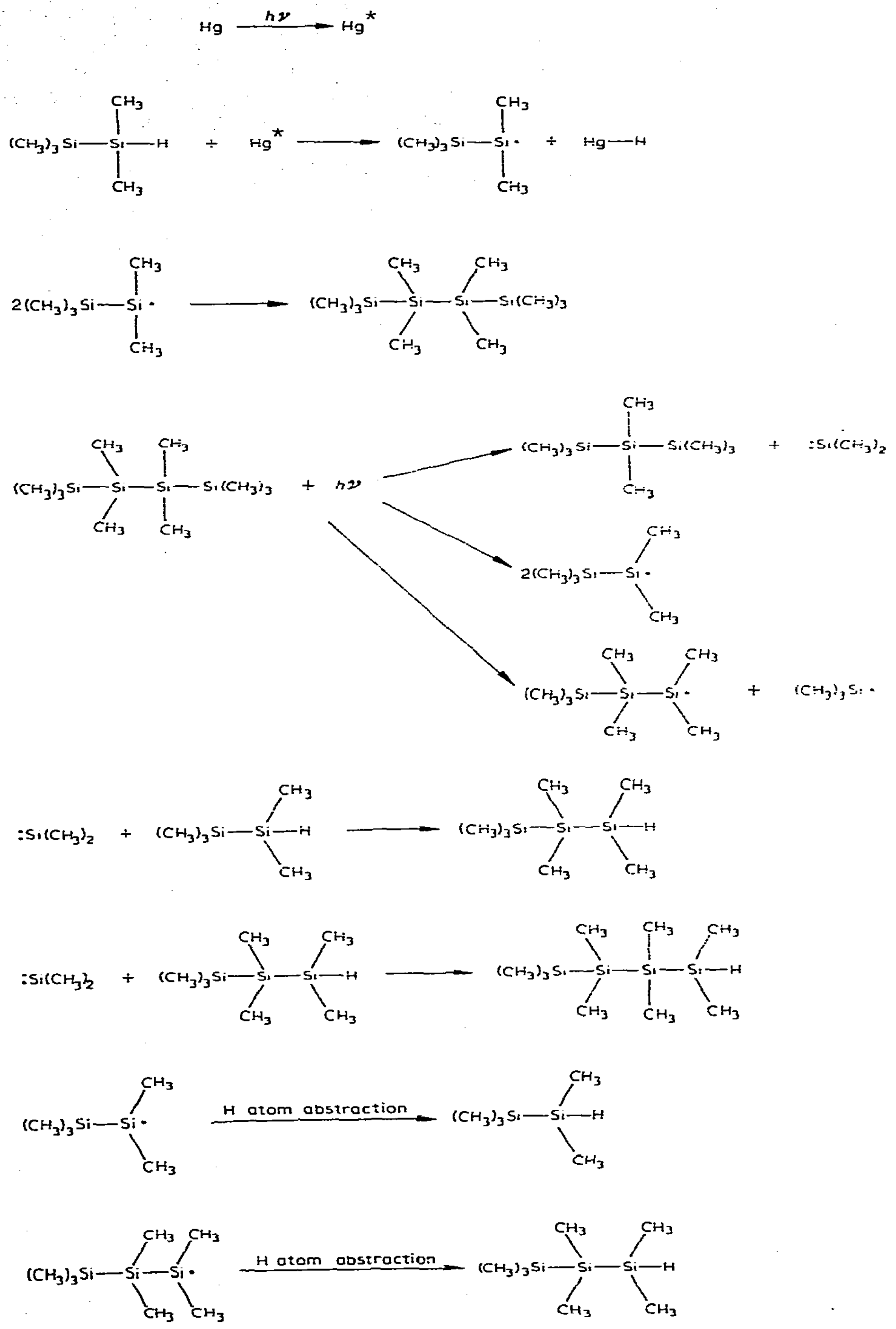
(CH_3—Si_4—CH_3) [7] (53%) and octamethyltrisilane (CH_3—Si_3—CH_3) [8] (21%) as the major products. Photolysis of H—Si_2—H [9] yields 1,3-dihydrohexamethyltrisilane (H—Si_3—H) [10] (37%) and 1,4-dihydrooctamethyltetrasilane (H—Si_4—H) [10] (44%).

These results are unusual in that all previous work has reported that photolysis of polysilanes results in degradation of the starting polysilane to yield a smaller polysilane and a silylene or smaller 1-hydropolysilanes. Photolysis of linear permethylated polysilanes $CH_3[Si(CH_3)_2]_nCH_3$ from $n = 4$ to $n = 8$ in solution proceeds by two pathways: the first involves contraction of the polysilane chain with loss of dimethylsilylene to ultimately produce CH_3—Si_3—CH_3 (which is stable to photolysis) while the second involves homolytic scission of a Si—Si bond followed by hydrogen abstraction by the silyl radicals to form 1-hydropermethylpolysilanes [11,12]. Similarly, photolysis of dodecamethylcyclohexasilane yields dimethylsilylene and decamethylcyclopentasilane and octamethylcyclotetrasilane [13,14]. Even photolysis of certain trisilanes in solution results in extrusion of the central silicon atom as a silylene with simultaneous formation of a disilane. Photolysis of 1,2,3-trisilacycloheptanes yields 1,2-disilacyclohexanes and a silylene [15,16]. Likewise, photolysis of heptamethyl-2-phenyltrisilane yields hexamethyldisilane and methylphenylsilylene [17,18].

A reaction sequence which accounts for the formation of CH_3—Si_3—CH_3 (21%) and CH_3—Si_4—CH_3 (53%) from the mercury sensitized photolysis of CH_3—Si_2—H is presented in Scheme 1. Interaction of a photoexcited mercury atom with CH_3—Si_2—H results in homolytic cleavage of the Si—H bond and formation of a pentamethyldisilyl radical. Coupling of two pentamethyldisilyl radicals yields CH_3—Si_4—CH_3. The reaction is run in the vapor phase at 105° C. The product, CH_3—Si_4—CH_3, rapidly condenses into the liquid phase which is protected from light. However, if it absorbs a photon of light in the vapor phase or while it is draining down the walls of the photolysis vessel it may fragment to yield CH_3—Si_3—CH_3 and dimethylsilylene or by homolytic scission of a Si—Si bond to yield a pair of silyl radicals. The first pathway has been shown to be the most important in the solution phase photolysis of CH_3—Si_4—CH_3 [12]. The fate of the dimethylsilylene thus produced has only been partially determined. Dimethylsilylene is known to insert into Si—H bonds [14,16,19—21]. Insertion of dimethylsilylene into the Si—H bond of CH_3—Si_2—H will yield 1-hydroheptamethyltrisilane (CH_3—Si_3—H) (1%) [22]. Further, insertion of dimethylsilylene into the Si—H bond of CH_3—Si_3—H will yield 1-hydrononamethyltetrasilane (CH_3—Si_4—H) (5%) [23]. It was expected that CH_3—Si_3—H would be formed in approximately equal amount to CH_3—Si_3—CH_3 since CH_3—Si_2—H is present in high concentration. Possibly the Si—H bond of CH_3—Si_3—H is more reactive than the Si—H bond of CH_3—Si_2—H. Dimethylsilylene may also polymerize or react with the surface of the quartz photolysis vessel. Approximately 0.9 g of meterial could not be easily removed from the photolysis apparatus after each reaction, an observation which may be consistent with this suggestion. Homolytic scission of a Si—Si bond is a minor pathway (11%) in the solution phase photolysis of CH_3—Si_4—CH_3 [12]. Cleavage of the central Si—Si bond will yield a pair of pentamethyldisilyl radicals which may yield CH_3—Si_2—H by hydrogen abstraction from other molecules in the system. Cleavage of a terminal Si—Si bond will yield a trimethylsilyl radical and a heptamethyltrisilyl radical pair. Scission

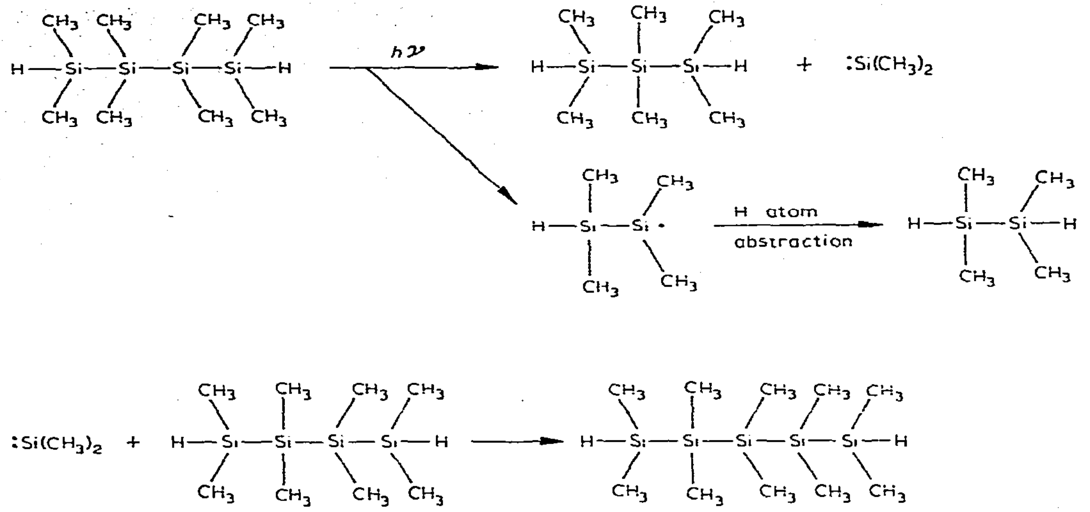


SCHEME 1. Mercury sensitized photolysis of pentamethyldisilane.

of a terminal Si—Si bond is less facile than scission of an internal Si—Si bond [12]. Trimethylsilane probably would have been lost under our reaction conditions. Hydrogen abstraction by the heptamethyltrisilyl radical provides another pathway to CH_3—Si_3—H. Several other minor products were detected by GLC but were not identified.

Mercury sensitized photolysis of H—Si_2—H at 105° C in the vapor phase yields H—Si_3—H (37%) and H—Si_4—H (44%). No other volatile products were detected. Since H—Si_3—H and H—Si_4—H may be easily separated by distillation, this reaction is of some preparative value. The ratio of H—Si_3—H to H—Si_4—H was constant throughout the photolysis. The possibility that H—Si_3—H was formed by a thermal reaction of H—Si_4—H and H—Si_2—H was ruled out by control experiments: a 1 : 1 molar mixture of H—Si_4—H and H—Si_2—H was heated at 105° C both in the presence of mercury and in its absence for 20 h. Neither H—Si_3—H nor any change in the starting materials could be detected at the end of this time by GLC. The formation of these two products may be explained by an analogous sequence of reactions. Interaction of a photoexcited mercury atom with H—Si_2—H results in homolytic cleavage of one Si—H bond and formation of a 1-hydrotetramethyldisilyl radical. Coupling of two such radicals yields H—Si_4—H. Photolysis of H—Si_4—H results in H—Si_3—H and dimethylsilylene or in homolytic scission of the central Si—Si bond to yield a pair of 1-hydrotetramethyldisilyl radicals. Insertion of dimethylsilylene into the Si—H bond of H—Si_2—H yields H—Si_3—H [19—21], while insertion of dimethylsilylene into an Si—H bond of H—Si_3—H regenerates H—Si_4—H. Thus, this experiment gives us no measure of the relative reactivities of the Si—H bond of a disilane versus the Si—H bond of a trisilane. Polymerization of dimethylsilylene or reaction with the surface of the quartz photolysis vessel may explain the observation that about one gram of material could not be easily removed from the vessel at the end of the reaction. The pentamethyldisilyl radicals produced by homolytic scission of the central Si—Si bond yield H—Si_2—H by hydrogen atom abstraction from other molecules in the system.

This pathway was verified by photolysis of H—Si_4—H in the vapor phase in the absence of H—Si_2—H. The photolysis of H—Si_4—H has not been previously reported. The observed products and their ratios are similar whether the photolysis is carried out in the presence or absence of mercury. Thus, mercury sensitization is probably not important, The major products are H—Si_2—H, H—Si_3—H, recovered H—Si_4—H, 1,5-dihydrodecamethylpentasilane (H—Si_5—H) [24] and polymer. The formation of these products is outlined in Scheme 2. Photolysis of H—Si_4—H proceeds by two pathways: one yields H—Si_3—H and dimethylsilylene, while the other involves scission of the central Si—Si bond to yield a pair of 1-hydrotetramethyldisilyl radicals. Hydrogen atom abstraction by a 1-hydrotetramethyldisilyl radical yields H—Si_2—H. The photolysis was carried out under reduced pressure so that H—Si_3—H and H—Si_2—H were pumped out of the photolysis zone and into a cold trap at —78° C soon after their formation. For this reason, dimethylsilylene reacts with the Si—H bond of H—Si_4—H to yield H—Si_5—H which condenses. However, dimethylsilylene must undergo other reactions since the yield of H—Si_3—H is higher than the yield of H—Si_5—H. The yield of H—Si_3—H may reflect the amount of dimethylsilylene initially produced, while the yield of H—Si_2—H may reflect the extent of homolytic scission of the



SCHEME 2. Photolysis of 1,4-Dihydrooctamethyltetrasilane.

central Si—Si bond of H—Si_4—H. The formation of some polymer is not unexpected for a difunctional compound in the presence of free radicals.

Experimental

Starting materials and products are all known compounds. The photolysis products were isolated from the reaction mixtures by preparative GLC and their identities checked by comparison of their spectral properties with literature values, and by mass spectrometry. Vapor phase chromatography was carried out on a Hewlett—Packard F&M 700 using a 1/4" × 4' 20% polyphenylether on 60/80 mesh Chromosorb P at 150°C. Infrared spectra were obtained on a Perkin—Elmer 337 spectrometer and were calibrated against known bands in a polystyrene film. NMR spectra were recorded on a Varian T-60 spectrometer or a Varian XL-100. Ten percent solutions in carbon tetrachloride with methylene chloride as internal standard (δ 5.30) were used for spectra run on the T-60. Spectra run on the XL-100 used deuterio chloroform as lock signal. Mass spectra were obtained on a Hitachi—Perkin—Elmer RMU-6E spectrometer at an ionizing voltage of 70 eV. Ultraviolet spectra were obtained on a Beckman Acta M spectrometer in spectrograde cyclohexane.

Photolysis of pentamethyldisilane

Pentamethyldisilane [5] 8.5 g (64.4 mmol), NMR (δ, ppm): 0.12 (s, 9H), 0.13 (d, 6H, J 4.5 Hz), 3.65 (septet, 1H, J 4.5 Hz [26]), 1 drop of mercury and a teflon covered magnetic stirring bar were placed in a dry 500 ml cylindrical (Ø 5 cm, length 45 cm) quartz vessel. The vessel was placed at the center of a circular array of sixteen 12" G.E. germicidal lamps 2537 Å. The quartz vessel was connected to a water cooled reflux condenser topped with a nitrogen inlet. The entire system was flushed with purified nitrogen for 20 min. The bottom of the vessel was heated at 105° C using a heating mantle. The liquid was stirred with a magnetic stirring bar. The liquid was protected from direct irradiation. The vapor was photolyzed for 18 h, after which the solution was decanted from the mercury and the stirring bar. The vessel was rinsed with 5 ml of ether. The ether was removed from the combined organic layer by distillation through a 10 cm Vigreux column. The residue weighed 8.0 g (94% recovery). It was bulb to bulb distilled at 120° C/0.1 mmHg. The non-volatile residue weighed 1.0 g. The volatile material was analyzed by GLC. The following compounds were identified and samples were isolated by preparative GLC for spectral identification: CH_3—Si_3—CH_3 (21%): NMR (δ, ppm): 0.02 (s, 6H), 0.03 (s, 18H); mass spectrum parent at *m/e* 204 (6%); UV: λ_{max} 2176 Å, ϵ 6.57 × 10^3 (Lit. [25] λ_{max} 2150 Å, ϵ 9.02 × 10^3); CH_3—Si_4—CH_3 (53%): NMR (δ, ppm): 0.08 (s, 18H), 0.1 (s, 12H); mass spectrum parent at *m/e* 262 (1.3%); UV: λ_{max} 2355 Å, ϵ 1.41 × 10^4 (Lit. [25] λ_{max} 2350 Å, ϵ 1.47 × 10^4); 1-hydroheptamethyltrisilane (1%): NMR (δ, ppm): 0.18 (s, 9H), 0.20 (s, 6H), 0.21 (d, 6H, *J* 5 Hz), 3.75 (septet, 1H, $J = 5$ Hz) mass spectrum parent at *m/e* 190 (2.1%); IR: Si—H 2088 cm^{-1}; 1-hydrononamethyltetrasilane (5%) [20]: NMR (δ, ppm): 0.04 (s, 9H), 0.06 (s, 6H), 0.09 (s, 6H), 0.09 (d, 6H, *J* 5 Hz), 3.93 (septet, 1H, *J* 7 Hz); mass spectrum parent at *m/e* 248 (0.2%); IR: Si—H 2086 cm^{-1}.

Photolysis of sym-tetramethyldisilane

sym-Tetramethyldisilane ([9] NMR (δ, ppm): 0.11 (d, 12H, *J* 4.7 Hz); [26] 3.8 (m, 2H)) and a drop of mercury were placed in the quartz vessel previously described. The solution was heated at 105° C for 18 h while being photolyzed at 2537 Å. At the end of this time, the solution was worked up as previously described. The residue weighed 9.3 g. It was bulb to bulb distilled at 110° C/0.2 mmHg. The non-volatile material weighed 1.1 g. The volatile material was analyzed by GLC. The following compounds were isolated by preparative GLC for spectral identification. H—Si_3—H (37%) [10]: NMR (δ, ppm): 0.13 (s, 6H), 0.12 (d, 12H, *J* 5 Hz); 3.73 (septet, 2H, *J* 5 Hz); mass spectrum at parent *m/e* 176 (2.0%); IR: Si—H 2090 cm^{-1}; UV: λ_{max} 2180 Å, ϵ 8.10 × 10^3 (Lit. [24] λ_{max} 2180 Å, ϵ 6.84 × 10^3); and H—Si_4—H (44%) [10]: NMR (δ, ppm): 0.12 (d, 12H, *J* 5 Hz), 0.13 (s, 12H), 3.78 (septet, 2H, *J* 5 Hz); mass spectrum parent at *m/e* 234 (2.0%); IR: Si—H 2095 cm^{-1}; UV: λ_{max} 2364 Å, ϵ 1.24 × 10^4 (Lit. [24] λ_{max} 2355 Å, ϵ 1.23 × 10^4). The volatile residue was fractionated through a 15 cm Vigreux column to give 3.7 g of H—Si_3—H, b.p. 56° C/19 mmHg (Lit. [10] b.p. 54° C/22 mmHg) and 4.4 g of H—Si_4—H, b.p. 83° C/19 mmHg (Lit. [10] b.p. 74° C/9 mmHg).

Photolysis of 1,4-dihydrooctamethyltetrasilane under reduced pressure

The same photolysis apparatus as previously described was used, except that an additional Dry-Ice/acetone trap was placed between the water condenser and a vacuum pump. In the quartz photolysis vessel was placed 6.8 g of H—Si_4—H [10], two drops of mercury, and a 1/2″ teflon covered magnetic stirring bar. The system was flushed with dry nitrogen for 20 min before the vacuum pump was turned on. The pressure in the system was maintained at 15—20 mmHg by use of a manostat throughout the photolysis. The solution was heated with stirring and the refluxing vapor (110° C) was photolyzed for 21 h. The solution was decanted. It weighed 3.8 g. A bulb to bulb distillation of this solution at 110° C/0.1 mmHg gave 2.5 g of volatile material. This was shown by GLC to be a mixture of H—Si$_4$—H (24%) and H—Si$_5$—H (12%) [24]: NMR (δ, ppm): 0.06 (s, 6H), 0.16 (s, 12H), 0.17 (d, 12H, J 5 Hz), 3.74 (septet, 2H, J 5 Hz); mass spectrum parent at *m/e* 292 (1.6%); IR: Si—H 2090 cm^{-1}; UV: λ_{max} 2152 and 2499 Å, ϵ 9.45 × 10^3 and 1.13 × 10^4 (Lit. [24] λ_{max} 2140 and 2490 Å, ϵ 9.44 × 10^3 and 1.36 × 10^4). The solution trapped in the Dry-Ice/acetone trap weighed 2.5 g. It was shown to be a mixture of H—Si$_2$—H (8.5%), and H—Si$_3$—H (30%). Identical results were obtained from a similar photolysis carried out without mercury.

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