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PHOTOLYSIS OF ARYL-SUBSTITUTED DISILANES IN THE PRESENCE OF DIMETHYL SULFOXIDE

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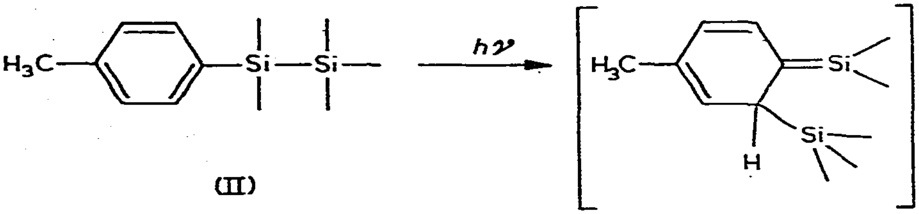
Summary

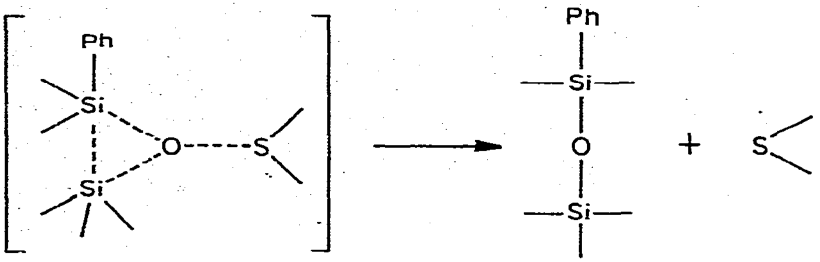
The photolysis of aryl-substituted disilanes in the presence of dimethyl sulfoxide has been studied. The products are found to be disiloxanes, aryl-substituted silanes, dimethylsilanone [$(CH_3)_2Si{=}O$], and dimethyl sulfide. Possible mechanisms for these reactions are discussed.

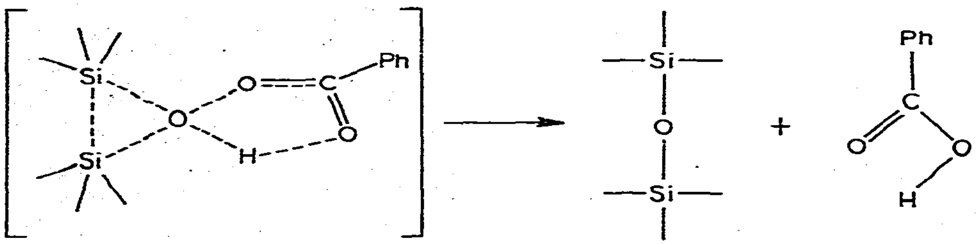
Two major pathways involving formation of intermediates possessing reactive silicon—carbon double bonds have been observed in the photolysis of aryl-substituted disilanes. Thus photolysis of methylpentaphenyldisilane in methanol-O-d_1 yields triphenylsilane and methoxymethyl-d_1-diphenylsilane in equal amounts. This result has been interpreted in terms of initial formation of triphenylsilane and the reactive intermediate 1,1-diphenylsilamethylene by an intramolecualr pathway. Subsequent reaction of 1,1-diphenylsilamethylene with methanol-O-d_1 yields methoxymethyl-d_1-diphenylsilane [1]. On the other hand, Kumada and co-workers have extensively studied the photochemical behavior of pentamethylphenyldisilane (I) and pentamethyl-p-tolyldisilane (II). A reactive intermediate possessing a silicon—carbon double bond is formed in this case by a 1,3-sigmatropic rearrangement of the terminal trimethylsilyl group from silicon to a carbon atom in an *ortho* position of the p-tolyl ring. Reactions of this intermediate have been studied with acetylenes [2], alkenes [3], dienes [4], and methanol-O-d_1 [5].



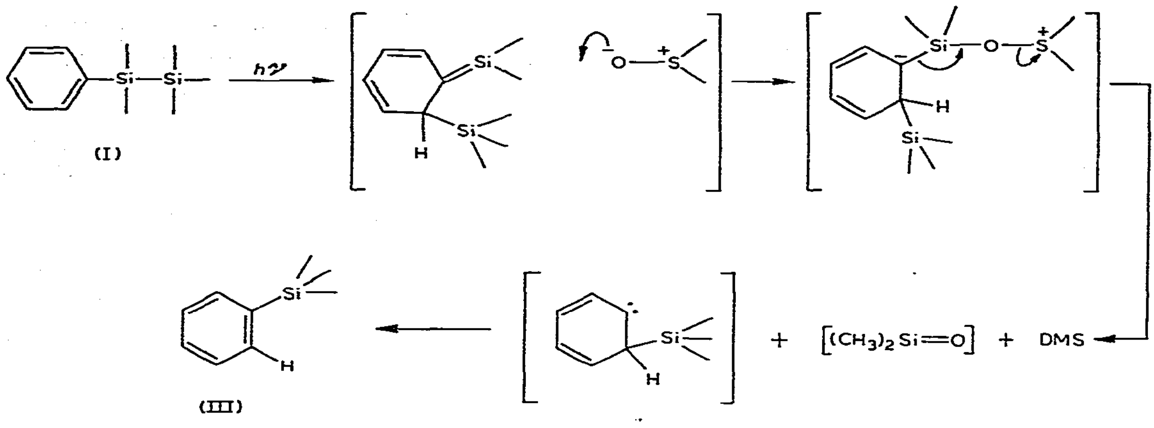
We have found that photolysis of aryl-substituted disilanes in the presence of one equivalent of dimethyl sulfoxide (DMSO) in dioxane as solvent takes very different pathways. For example, photolysis of a deoxygenated solution composed of 1 mmol each of I and DMSO, and 20 mmol of dioxane for 1 hour at 5°C with a 450 W medium pressure Hanovia Hg lamp results in a 95% consumption of I and formation of trimethylphenylsilane (III, 56%), pentamethylphenyldisiloxane (IV, 44%), dimethyl sulfide (DMS) (90%), and a 56% yield of dimethylsilicone oligomers. Similar results were obtained when the solution was photolyzed at 20°C in the center of a circular array of 16 12-in G.E. germicidal low pressure mercury lamps (2537 Å).

The formation of IV and an equal amount of DMS may be explained by a direct oxidation of the photoexcited Si—Si single bond by DMSO. These aryldisilanes are stable to DMSO in the absence of light. This reaction may be related to the direct oxidation of Si—Si single bonds by perbenzoic acid [6—8].

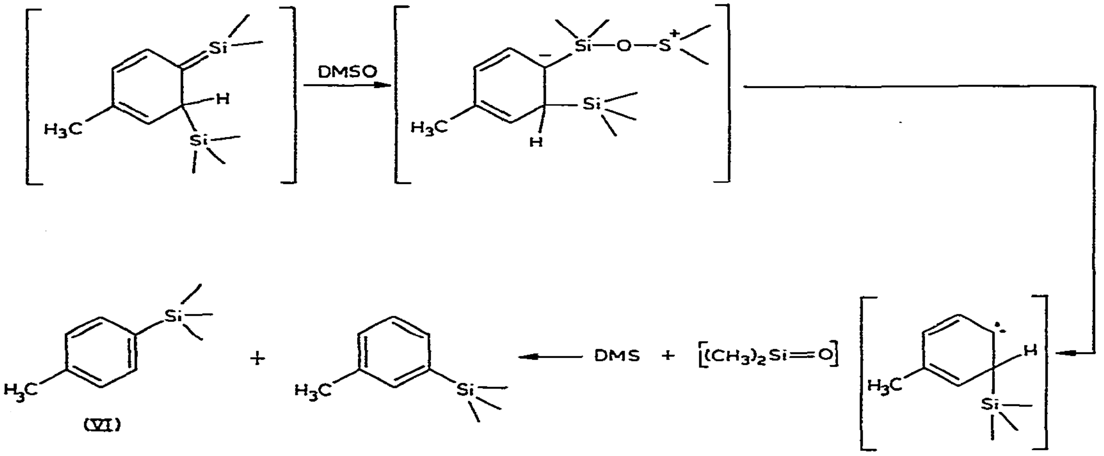




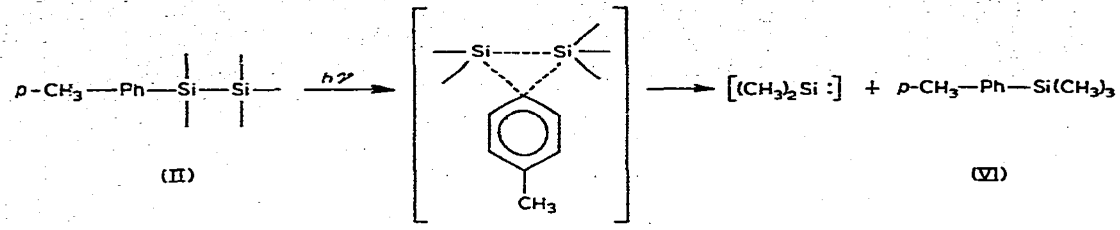
The second process, the formation of III, DMS, and dimethylsilicone oligomers is more complicated. The first mechanistic possibility involves a Kumada-type intermediate possessing a silicon—carbon double bond. Nothing is known concerning the reactions of silicon—carbon double-bonded intermediates with DMSO. The formation of the products observed can be rationalized as follows: nucleophilic attack by the oxygen of DMSO on the silicon of the silicon—carbon double-bonded intermediate leads to a zwitterionic intermediate which decomposes to yield DMS, dimethylsilanone which oligomerizes, and a carbenoid intermediate which rearranges to III by a 1,2-shift of a trimethylsilyl group or a hydrogen.



The photolysis of II in the presence of one equivalent of DMSO provides evidence against this possibility since only pentamethyl-*p*-tolyldisiloxane (V, 25%), trimethyl-*p*-tolylsilane (VI, 75%), DMS (95%), and dimethylsilicone oligomers were formed. It is predicted that if a Kumada-type intermediate were involved both trimethyl-*m*-tolylsilane and VI would be formed since one would expect the 1,2 migration of a trimethylsilyl group or a hydrogen to a carbenoid center to be competitive. However, nothing is known concerning such migratory aptitudes.



An alternative possibility is a 1,2-migration of the aryl group to the adjoining silicon atom with loss of dimethylsilylene (VII). Subsequent reaction of VII with DMSO would yield dimethylsilanone and DMS. Free VII, generated by photolysis of dodecamethylcyclohexasilane, has previously been shown to react with DMSO to yield DMS and dimethylsilanone [9]. This would be followed by olgomerization of the dimethylsilanone. Several pieces of evidence weigh against this possibility. While photolysis of 2-phenylheptamethyltrisilane has been shown to yield methylphenylsilylene and hexamethyldisilane [10], this type of process has been previously shown to be quite unimportant (<3%) in the photolysis of I [5]. Further, photolysis of a mixture of I, DMSO, and diisopropylmethylsilane in dioxane gave no 1,1-diisopropyl-1,2,2-trimethyldisilane, the expected product of trapping of VII [5,11—13]. In control experiments, diisopropylmethylsilane was shown to be an efficient (>47%) trap for VII generated by photolysis of dodecamethylcyclohexasilane. Finally, hexamethylcyclotrisiloxane (VIII) has been shown to be a moderately efficient trapping reagent for not only dimethylsilanone to yield octamethylcyclotetrasiloxane (IX) but also for VII to yield 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxo-1,2,4,6-tetrasilacycloheptane (X) [9]. In experiments carried out with added VIII, no X was isolated. For these reasons, a mechanism involving free VII seems improbable.


(II)

(VI)

$$[(CH_3)_2Si:] + DMSO \longrightarrow [(CH_3)_2Si{=}O] + DMS$$

The following additional data must be included in any mechanistic scheme. Photolysis of tetramethyl-1,2-diphenyldisilane in the presence of one equivalent of DMSO yields dimethyldiphenylsilane (56%) and *sym*-tetramethyldiphenyldisiloxane (44%), DMS (92%), and dimethylsilicone oligomers. On the other hand, photolysis of tetramethyl-1,1-diphenyldisilane in the presence of one equivalent of DMSO yields III (47%), tetramethyl-1,1-diphenyldisiloxane (XI) (53%), DMS (93%), and methylphenylsilicone oligomers. Apparently, only an

TABLE 1

PHOTOLYSIS OF ARYLDISILANES WITH DMSO

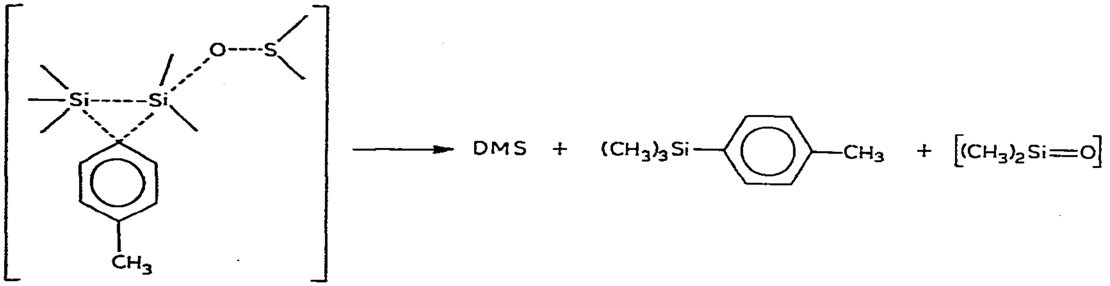
Conditions: 5°C, disilane (1 mmol), DMSO (1 mmol), dioxane (20 mmol), and time 60 min.

Starting material	Product (yields (%))	Conversion of disilane ^{a}(
$Ph(CH_3)_2SiSi(CH_3)_3$	$PhSi(CH_3)_3$ (56) $Ph(CH_3)_2SiOSi(CH_3)_3$ (44)	95
$Ph_2CH_3SiSi(CH_3)_3$	$PhSi(CH_3)_3$ (47) $Ph_2CH_3SiOSi(CH_3)_3$ (53)	80
$Ph(CH_3)_2SiSi(CH_3)_2Ph$	$Ph_2Si(CH_3)_2$ (56) $Ph(CH_3)_2SiOSi(CH_3)_2Ph$ (44)	87
p-$CH_3Ph(CH_3)_2SiSi(CH_3)_3$	p-$CH_3PhSi(CH_3)_3$ (75) p-$CH_3Ph(CH_3)_2SiOSi(CH_3)_3$ (25)	95

[a] Yields of DMS equal to amount of disilane consumed by NMR.

aryl group migrates from one silyl center to the other. Table 1 summarizes these results.

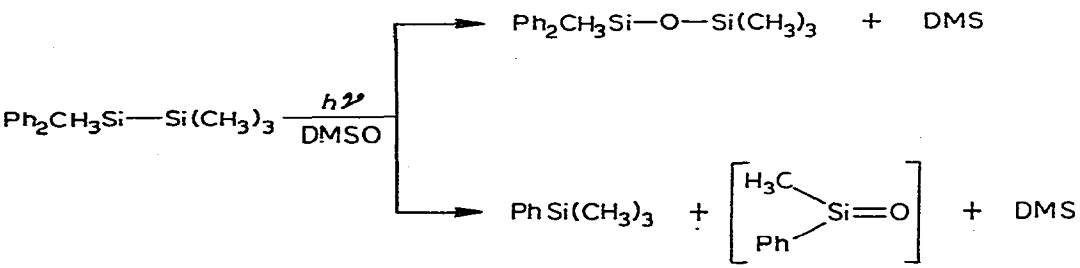
On the basis of these data, we propose the following mechanism. Attack by the nucleophilic oxygen of DMSO on the photoexcited disilane occurs at the silyl center bearing an aryl group. This causes the aryl group to migrate to the other silicon atom, resulting in formation of DMS, dimethylsilanone and an aryl-substituted silane in a single step.



To test for the intermediacy of dimethylsilanone, similar photolysis reactions have been carried out in the presence of VIII which is known to react with dimethylsilanone to yield IX [14,15]. A major problem in this area is that while VIII will trap dimethylsilanone, it is certainly not as efficient as one would like.

Photolysis of II (1 mmol), DMSO (1 mmol), VIII (3 mmol), and dioxane (20 mmol) for one hour resulted in a 95% consumption of the starting disilane. The following products were isolated VI (7.5%), V (25%), DMS (91%), IX (8%), and recovered VIII (91%). The presence of VIII has not appreciably disturbed the photolysis since the ratio of VI to V is virtually unchanged. However, our efficiency in trapping dimethylsilanone is only 8%. The major pathway for dimethylsilanone under these conditions is self-oligomerization.

The photolysis of tetramethyl-1,1-diphenyldisilane (1 mmol), DMSO (1 mmol), VIII (3 mmol), and dioxane (20 mmol) for one hour yields particularly interesting results. The products of this reaction are III (45%), XI (55%), DMS (>95%), heptamethylphenylcyclotetrasiloxane (14%), recovered VIII (80%), and methylphenylsilicone oligomers. In the photolysis of tetramethyl-1,1-diphenyldisilane, methylphenylsilanone is lost rather than dimethylsilanone. Control reactions in the presence of diisopropylmethylsilane gave no 1,1-diisopropyl-1,2-dimethyl-2-phenyldisilane, the expected product of insertion of methylphenylsilylene into the Si—H bond of diisopropylmethylsilane.



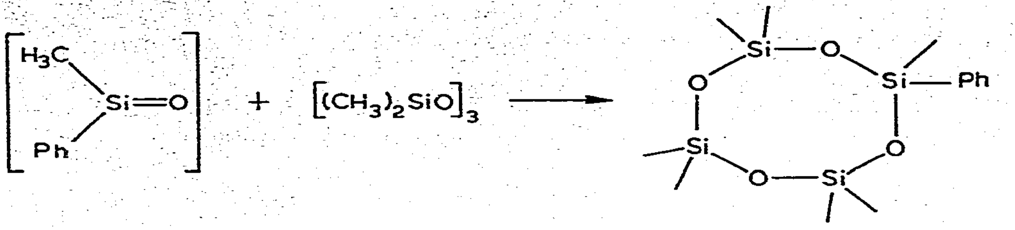


TABLE 2

PHOTOLYSIS OF ARYLDISILANES WITH DMSO AND $[(CH_3)_2SiO]_3$

Conditions: 5°C, disilane (1 mmol), DMSO (1 mmol), $[(CH_3)_2SiO]_3$ (3 mmol), dioxane (20 mmol), time 60 min.

Starting material	Product (yields (%))	Conversion of disilane (%) [a]	Recovery of $[(CH_3)_2SiO]_3$ (%)
$Ph(CH_3)_2SiSi(CH_3)_3$	$PhSi(CH_3)_3$ (61) $Ph(CH_3)_2SiOSi(CH_3)_3$ (39) $[(CH_3)_2SiO]_4$ (14)	94	5
$Ph_2CH_3SiSi(CH_3)_3$	$PhSi(CH_3)_3$ (45) $Ph_2CH_3SiOSi(CH_3)_3$ (55) $(PhCH_3SiO)[(CH_3)_2SiO]_3$ (14)	88	80
$Ph(CH_3)_2SiSi(CH_3)_2Ph$	$Ph_2Si(CH_3)_2$ (57) $Ph(CH_3)_2SiOSi(CH_3)_2Ph$ (43) $[(CH_3)_2SiO]_4$ (36)	80	9
p-$CH_3Ph(CH_3)_2SiSi(CH_3)_3$	p-$CH_3PhSi(CH_3)_3$ (75) p-$CH_3Ph(CH_3)_2SiOSi(CH_3)_3$ (25) $[(CH_3)_2SiO]_4$ (8)	95	91

[a] Yields of DMS equal to amount of disilane consumed by NMR.

One final problem must be mentioned. Our recovery of VIII is not as good in every case. Control experiments have shown that VIII is stable on photolysis in the presence of DMSO in dioxane solution. Nevertheless, photolysis of I (1 mmol), DMSO (1 mmol), VIII (3 mmol) in dioxane (20 mmol) leads to III (61%), IV (39%), DMS (93%), IX (14%), and recovered VIII (5%). Clearly, VIII is undergoing co-oligomerization with dimethylsilanone in this experiment. Table 2 summarizes these results.

In conclusion, two new photochemical pathways for aryldisilanes have been observed. Both involve nucleophilic attack by the oxygen of the DMSO on the photoexcited aryldisilane. The first involves direct attack on the Si—Si single bond to yield an aryl-substituted disiloxane and DMS. The second involves attack on the aryl-substituted silyl center leading to migration of the aryl group from one silicon to the other with formation of dimethylsilanone, DMS and an aryl-substituted silane. Attack by solvent methanol on photoexcited organosilicon molecules have been previously observed [5,16].

Experimental

IR spectra were determined as neat liquids on a Perkin—Elmer 281. NMR spectra were recorded on a Varian T-60 or XL-100 spectrometer. Spectra were taken using 10% solutions in CCl_4 with an internal standard of cyclohexane. Samples of all compounds for spectral and elemental analysis were purified by preparative vapor phase chromatography on a Hewlett—Packard F & M 700. Yields of various products were determined by GLPC except for dimethyl sulfide which was determined by NMR. Mass spectra were determined on a DuPont 21-492 at 70 eV. Microanalysis was performed by the Cal. Tech. Microanalytical Laboratory, Passadena, California.

Virtually all of the starting materials and products are known compounds. They were prepared following literature methods. They has physical and spectral properties in full agreement with literature values. In those cases where NMR spectra have not been previously reported we have included these data.

Pentamethylphenyldisilane [17]. NMR δ 7.41—7.02 (m, 5H), 0.33 (s, 6H), 0.06 (s, 9H) ppm.

Tetramethyl-1,1-diphenyldisilane [17]. NMR δ 7.50—7.03 (m, 10H), 0.60 (s, 3H), 0.18 (s, 9H) ppm.

sym-Tetramethyldiphenyldisilane [17]. NMR δ 7.13 (s, 10H), 0.33 (s, 6H) ppm.

Pentamethyl-*p*-tolyldisilane [4].

Trimethylphenylsilane [18].

Trimethyl-*p*-tolylsilane [5,19].

Trimethyl-*m*-tolylsilane [19]. NMR δ 7.34—6.73 (m, 4H), 2.42 (s, 3H), 0.33 (s, 9H) ppm.

Dimethyldiphenylsilane [20]. NMR δ 7.48—7.05 (m, 10H), 0.54 (s, 6H) ppm.

Diisopropylmethylsilane [21]. NMR δ 3.60—3.20 (m, 1H), 0.99 (br, s, 14H), 0.00 (d, 3H, J 3.2 Hz) ppm.

Hexamethylcyclotrisiloxane (Silar Laboratories). Its purity was checked by GLPC on three 1/4" × 30" columns packed with 20% SE-30, 20% polyphenyl ether or 20% FFAP on Chromosorb P. Under all of these conditions it was found to be pure and uncontaminated with octamethylcyclotetrasiloxane.

Octamethylcyclotetrasiloxane (Silar Laboratories). Its purity was checked as above.

Pentamethylphenyldisiloxane [22]. NMR δ 7.44—6.98 (m, 5H), 0.32 (s, 3H), 0.09 (s, 3H) ppm.

Tetramethyl-1,1-diphenyldisiloxane [22]. NMR δ 7.51—7.01 (m, 10H), 0.59 (s, 3H), 0.11 (s, 3H) ppm.

sym-Tetramethyldiphenyldisiloxane [23]. NMR δ 7.47—7.02 (m, 10H), 0.32 (s, 6H) ppm.

Heptamethylphenylcyclotetrasiloxane [24,25].

Pentamethyl-*p*-tolyldisiloxane was prepared by co-hydrolysis [22] of chlorodimethyl-*p*-tolylsilane [26] and trimethylchlorosilane. It had the following properties: IR Si—O—Si 1055 cm^{-1}; NMR δ 7.23 (d, 2H, J 7.6 Hz), 6.93 (d, 2H, J 7.6 Hz), 2.34 (s, 3H), 0.31 (s, 6H), and 0.08 (s, 9H) ppm. Anal. Found: C, 60.10; H, 9.20. $C_{12}H_{22}Si_2O$ calcd.: C, 60.44; H, 9.30%.

1,1-Diisopropyl-1,2,2-trimethyldisilane. A solution of 0.26 g (0.75 mmol) of dodeamethylcyclohexasilane [27] and 0.39 g (3.0 mmol) of diisopropylmethylsilane is dissolved in 1.76 g (20 mmol) of dioxane in a quartz NMR tube. The solution was deoxygenated by bubbling purified nitrogen through it for 15 min prior to photolysis. This mixture was photolyzed at 5°C in an ice/water bath for 30 min using a 450 W medium pressure Hanovia Hg lamp. Analysis of the resulting colorless solution by GLPC on a 1/4" X 18" 20% SE-30 on Chromosorb P 60/80 mesh indicated a 47% yield of 1,1-diisopropyl-1,2,2-trimethyldisilane as well as diisopropylmethylsilane in 41% recovered yield. It has the folllowing properties: IR Si—H 2080 cm^{-1}, NMR δ 3.72 (sept, 1H), 1.03 (s, 14H), 0.20 (d, 6H J 50 Hz), 0.03 (s, 3H) ppm. Anal. Found: C, 57.19; H, 12.76. $C_9H_{24}Si_2$ calcd.: C, 57.36; H, 12.84%.

Dioxane was purified by distillation from lithium aluminum hydride immediate prior to use.

Dimethyl sulfoxide was stored over Drierite for several days. It was distilled under reduced pressure [28].

Photolysis of aryl substituted disilanes with DMSO

The following is a typical procedure. A mixture of I [17] 208 mg (1 mmol), DMSO 78 mg (1 mmol) and dioxane 1.76 (20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated by bubbling purified nitrogen through it for 15 min prior to irradiation with a 450 W medium pressure Hanovia Hg lamp for 60 min at 5°C in an ice water bath. GLPC analysis of the resulting yellow solution on a 1/4" X 30" 20% SE-30 Chromosorb P 60/80 mesh column showed the formation of III [7] (56%), IV [22] (44%) and recovered I (5%). Product yields are corrected for recovered starting material. NMR spectra of this mixture indicated formation of DMS in >90% yield. Trimethylphenylsilane, IV and recovered I were collected by preparative GLPC on the same column after bulb to bulb distillation under reduced pressure (1 mmHg). They were identified by comparison of their IR and NMR spectra and GLPC retention times with those of authentic samples. The residue from the bulb to bulb distillation, a viscous liquid was analyzed by IR and NMR spectra. It was identified as dimethylsilicone oligomers on the basis of its IR Si—O—Si broad peak centered at 1060 cm^{-1}, and NMR broad peak δ 0.09 ppm. The reactions of tetramethyl-1,1-diphenyldisilane, *sym*-tetramethyldiphenyldisilane, and pentamethyl-*p*-tolyldisilane with DMSO were carried out in a similar manner. The results are summarized in Table 1.

Photolysis of aryl-substituted disilanes with DMSO and hexamethylcyclotrisiloxane

A mixture of 208 mg I (1 mmol), 78 mg of DMSO (1 mmol), 666 mg of VIII (3 mmol), and 1.76 g of dioxane (20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated and photolyzed as above. The reaction mixture was analyzed by GLCP on a 1/4" X 30" 20% SE-30 on Chromosorb P column and on a 1/4" X 4' 20% Polyphenyl ether on Chromosorb P column. The products were identified by comparison of IR and NMR spectra and GLPC retention times with authentic samples. In a similar manner the reactions of tetramethyl-1,1-diphenyldisilane, *sym*-tetramethyldisilane, and II with DMSO in the presence of VIII were carried out. These results are summarized in Table 2.

Photolysis of I with DMSO and diisopropylmethylsilane

A mixture of 208 mg of I (1 mmol), 78 mg of DMSO (1 mmol), 390 mg of diisopropylmethylsilane (3 mmol) and 1.76 g of dioxane (20 mmol) was placed in a quartz NMR tube. This solution was deoxygenated and photolyzed as above. GLPC analysis of the reaction mixture on a 1/4" X 4' 20% polyphenyl ether column showed complete recovery of diisopropylmethylsilane, and formation of III (59%), IV (40%) and recovered I (7%). NMR of the solution showed production of DMS in greater than 95% yield.

Photolysis of DMSO and VIII

A solution of 78 mg of DMSO (1 mmol), 666 mg of VIII (3 mmol) and 1.76 g of dioxane (20 mmol) were placed in a quartz NMR tube. This solution was deoxygenated and photolyzed as above. Analysis by GLPC and NMR of the solution showed no reaction and complete recovery of starting materials.

Acknowledgement

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