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

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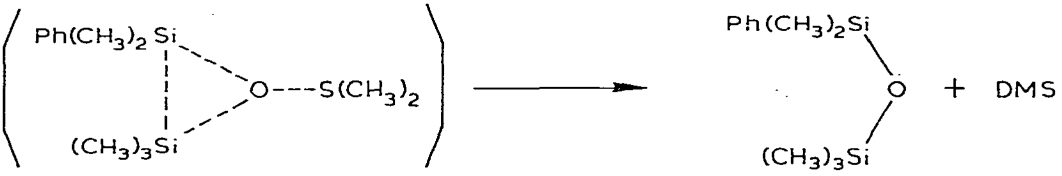
Summary

The photolysis of aryl-substituted disilanes in the presence of dimethyl sulfoxide has been studied. Product studies, labelling experiments, and quantum yields have been carried out. Possible mechanisms are discussed.

The photolysis of aryl-substituted disilanes in the presence of dimethyl sulfoxide (DMSO) has been reported [1]. While these results were basically correct, they were incomplete. We should like to remedy this situation.

Photolysis of pentamethylphenyldisilane (I), DMSO, and dioxane with monochromatic (2537 Å) light at 20°C yields the following volatile products: trimethylphenylsilane (II) (59%), pentamethylphenyldisiloxane (III) (32%), tetramethylsilane (IV) (3%), and dimethyl sulfide (DMS) ($\simeq$90%). All the products of this reaction and other reactions reported are stable under the photolysis conditions. We are not able to account for 100% of the material.

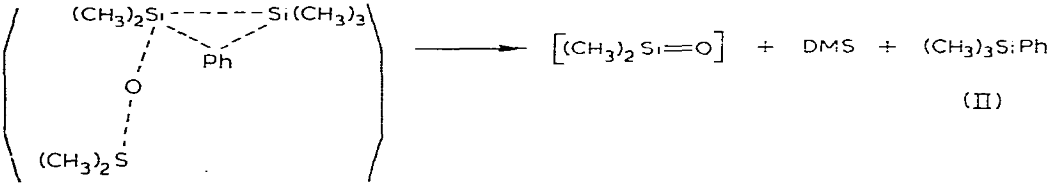
Formation of III and an equal amount of DMS may be explained by a direct oxidation of the photoexcited Si—Si single bond of I by DMSO. Control experiments have shown that the aryl-substituted disilanes discussed in this paper are stable to DMSO in the absence of light (8 h at 65°C).



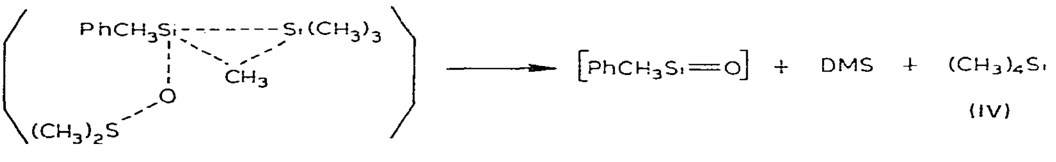
(III)

The formation of II and DMS may result from nucleophilic attack by the oxygen of DMSO on the dimethylphenylsilyl center of the photoexcited disilane.

This causes the phenyl group to migrate to the trimethylsilyl center to form II, DMS, and dimethylsilanone $[(CH_3)_2Si{=}O]$ in a single step. Independent evidence for the existence of dimethylsilanone in this reaction has been previously obtained by trapping reactions [1]. In the absence of trapping reagents, dimethylsilanone oligomerizes.



The formation of IV may be accounted for by a similar mechanism in which nucleophilic attack by the oxygen of DMSO on the dimethylphenylsilyl center causes migration of a methyl group to the trimethylsilyl center. This results in formation of IV, DMS, and methylphenylsilanone $[PhCH_3Si{=}O]$. No independent evidence for the formation of methylphenylsilanone has been obtained.



Photolysis of tetramethyl-1,1-diphenyldisilane (V) as above yields II (46%), tetramethyl-1,1-diphenyldisiloxane (VI) (33%), dimethyldiphenylsilane (VII) (5%), IV (2%), and DMS (≃90%).

The formation of VI probably occurs by direct oxidation of the photoexcited Si—Si single bond of V by DMSO. The formation of II may result from nucleophilic attack by the oxygen of DMSO on the methyldiphenylsilyl center resulting in migration of a phenyl group to the trimethylsilyl center and formation of methylphenylsilanone and DMS in a single step. Evidence for the existence of methylphenylsilanone in this reaction has been previously reported [1]. The formation of tetramethylsilane probably results from nucleophilic attack of the oxygen of DMSO on the methyldiphenylsilyl center resulting in migration of methyl group to the trimethylsilyl center and formation of diphenylsilanone $[Ph_2Si{=}O]$ and DMS in a single step. No independent evidence for the existence of diphenylsilanone has been obtained. Finally nucleophilic attack by the oxygen of DMSO on the trimethylsilyl center of the photoexcited disilane results in migration of a methyl group to the methyldiphenylsilyl center and formation of VII, dimethylsilanone, and DMS in a single step. No independent evidence for the existence of dimethylsilanone has been obtained.

Photolysis of *sym*-tetramethyldiphenyldisilane (VIII) as above yields *sym*-tetramethyldiphenyldisiloxane (IX) (25%), VII (45%), II (8%), hexamethyl-1,5-diphenyltrisiloxane (X) (7%), and DMS (≃90%).

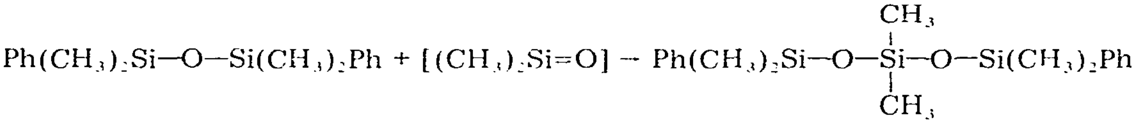
The formation of IX may be explained by a direct oxidation of the photoexcited Si—Si single bond of VIII by DMSO. The formation of VII may result from nucleophilic attack by the oxygen of DMSO on one of the dimethylphenylsilyl groups resulting in migration of a phenyl group to the other dimethyl-

TABLE I

QUANTUM YIELDS

Disilane	ϕ for disappearance of disilane	ϕ for appearance of major products			
		monosilane		disiloxane	
I	0.56	II	0.33	III	0.18
V	0.46	II	0.21	VI	0.15
VIII	0.52	VII	0.23	IX	0.13

phenylsilyl group and simultaneous formation of dimethylsilanone and DMS. Evidence for the formation of dimethylsilanone in this reaction has been previously obtained [1]. The formation of II probably results from nucleophilic attack by the oxygen of DMSO on one of the dimethylphenylsilyl groups resulting in methyl group migration to the other dimethylphenylsilyl center. No independent evidence for the formation of methylphenylsilanone has been obtained. Hexamethyl-1,5-diphenyltrisiloxane probably results from insertion of dimethylsilanone into one of the silicon—oxygen single bonds of IX. It is not present early in the photolysis of VIII.



$$Ph(CH_3)_2Si{-}O{-}Si(CH_3)_2Ph + [(CH_3)_2Si{=}O] \rightarrow Ph(CH_3)_2Si{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}Si(CH_3)_2Ph$$

(X)

The photo-oxidation of aryl-substituted disilanes in the presence of DMSO are efficient reactions. For this reason, the possibility of a radical chain process was considered. It was eliminated by a double labelling experiment. Photolysis of *sym*-tetramethyldiphenyl-d_{10}-disilane in the presence of DMSO yields *sym*-tetramethyldiphenyl-d_{10}-disiloxane and dimethyldiphenyl-d_{10}-silane in the same ratio as *sym*-tetramethyldiphenyldisilane. Photolysis of a 1/1 mixture of *sym*-tetramethyldiphenyldisilane and *sym*-tetramethyldiphenyl-d_{10}-disilane in the presence of DMSO was carried out as above. If the mechanisms previously proposed are correct, only *sym*-tetramethyldiphenyl-d_{10}-disiloxane, *sym*-tetramethyldiphenyldisiloxane, dimethyldiphenyl-d_{10}-silane, and dimethyldiphenylsilane should be formed. There should be no cross-over (d_5) products. Analysis of the products by mass spectroscopy indicated that no cross-over had occurred.

The disappearance of n-butyrophenone ($\phi = 0.33$) and the appearance of acetophenone ($\phi = 0.24$) in methylcyclohexane [7] was determined simultaneously with the photolysis of the aryl-substituted disilane to determine the light intensity for each kinetic run. The quantum yields for the disappearance of aryl-substituted disilanes, I, V, and VIII were determined (see Table I).

Experimental

IR spectra (Perkin—Elmer 281). NMR spectra (Varian T-60 or XL 100) were taken using 5% solution in $CDCl_3$ or DMSO-d_6. Samples for spectral analysis were purified by preparative GLPC on a Hewlett—Packard F & M 700. The following GLPC columns were used for analysis: 60″ × 0.25″ 20% SE-30 on Chromosorb W (A), 18″ × 0.25″ 20% SE-30 on Chromosorb W (B), and 132″ × 0.25″ 20% DCQF-1 on Chromosorb W (C). Yields were determined by GLPC using n-dodecane or cyclododecane as internal standard. Mass spectra (DuPont 21-492) were run at an ionizing voltage of 70 eV. UV spectra (Beckman Acta M) were determined in spectroquality cyclohexane. Product yields are corrected for recovered starting materials.

Virtually all of the compounds are known and were prepared by literature methods. They had the expected properties. In cases where spectral data have not been reported, we have included these data.

Pentamethylphenyldisilane [1,8]. Trimethylphenylsilane [9]. Tetramethylsilane [10]. Pentamethylphenyldisiloxane [1,11], Tetramethyl-1,1-diphenyldisiloxane [1,8]. Dimethyldiphenylsilane [1,12]. Tetramethyl-1,1-diphenyldisilane [1,11]. *sym*-Tetramethyldiphenyldisilane [1,8]. *sym*-Tetramethyldiphenyldisiloxane [1,13]. Hexamethyl-1,5-diphenyltrisiloxane [11] NMR δ 7.6—7.3 (m, 10 H), 0.29 (s, 12 H), 0.03 (s, 6 H) ppm.

sym-Tetramethyldiphenyl-d_{10}-disilane was prepared by addition of phenyl-d_5-magnesium bromide [14] to 1,2-dichlorotetramethyldisilane [15,16]. NMR: δ 0.35 (s) ppm. IR: ν(C—D) 2260 and 2295 cm^{-1}. UV: λ_{max} 2354, ϵ 16000. Mass spectrum: parent $C_{16}H_{12}D_{10}Si_2$ *m/e* 280 (27%), ($P-15$) *m/e* 265 (4%), *m/e* 140 (100%).

sym-Tetramethyldiphenyl-d_{10}-disiloxane. NMR: δ 0.31 (s) ppm. IR: ν(C—D) 2350 cm^{-1}. Mass spectrum: parent $C_{16}H_{12}D_{10}OSi_2$ *m/e* 296 (19%), ($P-15$) *m/e* 281 (100%), ($P-C_6D_5$) *m/e* 214 (13%).

Dimethyldiphenyl-d_{10}-silane. NMR: δ 0.56 (s) ppm. IR: ν(C—D) 2270 cm^{-1}. Mass spectrum: parent $C_{14}H_6D_{10}Si$ *m/e* 222 (18%), ($P-15$) *m/e* 205 (55%), ($P-C_6D_5$) *m/e* 140 (73%), *m/e* 110 (100%).

Dimethyl sulfoxide was stored over drierite and distilled from CaH_2 under reduced pressure immediately prior to use.

n-Dodecane was dissolved in CH_2Cl_2, washed free of alkenes with concentrated H_2SO_4 and then washed with water. The organic layer was separated and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the hydrocarbon was further purified by distillation through a 25 cm vacuum jacketed Vigreux column. B.p. 91°C/10 mmHg. Lit. [17] b.p. 94°C/13.5 mmHg.

Cyclododecane was purified as above. It was recrystallized from 95% ethanol. M.p. 60.5—61.5°C. Lit. [18] m.p. 61°C.

n-Butyrophenone was distilled before use. B.p. 122°C/25 mmHg.

Methylcyclohexane (spectroquality) (MC & B) was distilled before use.

Dioxane was distilled from $LiAlH_4$ immediately before use.

Photolysis of pentamethylphenyldisilane (I) with DMSO

A mixture of I (208 mg, 1 mmol), DMSO (18 mg, 1 mmol), cyclododecane (84 mg, 0.5 mmol) and dioxane (1.76 g, 20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated by bubbling purified nitrogen through it for 15 min. The tube was sealed with a rubber septum and irradiated in a quartz water jacket placed at the center of a circular array of sixteen 12″ G.E. Germicidal lamps (2537 Å) for 9 h. Cooling water was circulated through the water jacket. GLPC analysis of the resulting solution on column A showed the formation of II (59%), III (32%), and recovered I (24%). GLPC analysis of the same solution on column C indicated the formation of IV (3%). NMR spectra of this mixture indicated formation of DMS in >90% yield. All products were collected by preparative GLPC and identified by comparison of their NMR, IR, and GLPC retention times with those of authentic samples.

Photolysis of tetramethyl-1,1-diphenyldisilane (V) with DMSO

A mixture of V (270 mg, 1 mmol), DMSO (78 mg, 1 mmol), n-dodecane (85 mg, 0.5 mmol), and dioxane (1.76 g, 20 mmol) was photolyzed as above for 14 h. GLPC analysis of the resulting solution on column B indicated II (46%), VI (33%), VII (5%), and recovered V (5%), GLPC analysis on column C showed the formation of IV (2%). DMS was found in >90% yield (NMR).

Photolysis of sym-tetramethyldiphenyldisilane (VIII) with DMSO

A mixture of VIII (270 mg, 1 mmol), DMSO (78 mg, 1 mmol), n-dodecane (85 mg, 0.5 mmol) and dioxane (1.76 g, 20 mmol) was photolyzed as above for 12 h. GLPC analysis of the resulting solution on column B indicated II (8%), VII (45%), IX (25%), recovered VIII (12%), and X (7%). DMS was found in >90% yield (NMR).

Control experiment: Photolysis of sym-tetramethyldiphenyldisiloxane (IX) with DMSO

A mixture of IX 286 mg, 1 mmol), DMSO (78 mg, 1 mmol), n-dodecane (85 mg, 0.5 mmol) and dioxane (1.76 g, 20 mmol) was photolyzed as above for 8 h. GLPC on column B indicated the stability of IX (2.83 mg, 0.99 mmol, 99%).

In an analogous manner, the photochemical stabilities of II, III, VI, VII, and X were shown.

Control experiment: Thermolysis of pentamethylphenyldisilane (I) with DMSO

A mixture of I (208 mg, 1 mmol), DMSO (78 mg, 1 mmol), cyclododecane (84 mg, 0.5 mmol) and dioxane (1.76 mg, 20 mmol) was placed in an NMR tube, degassed by bubbling through prepurified nitrogen for 15 min, sealed with a rubber septum, and heated at 65°C for 8 h. GLPC analysis on column A showed only recovered starting materials and no formation of II or III.

In an analogous manner, the thermal stability of V and VIII were established.

Photolysis of sym-tetramethyldiphenyl-d_{10}-disilane with DMSO

A mixture of *sym*-tetramethyldiphenyl-d_{10}-disilane (28 mg, 0.1 mmol), DMSO (8 mg, 0.1 mmol), and dioxane (176 mg, 2 mmol) was placed in a quartz NMR tube. The solution was deoxygenated, sealed with a rubber septum, and was irradiated for 60 min at 5°C. GLPC analysis of the resulting solution on column B showed the formation of dimethyldiphenyl-d_{10}-silane and *sym*-tetramethyldiphenyl-d_{10}-disiloxane in a ratio of 58 to 42.

Co-photolysis of sym-tetramethyldiphenyl-d_{10}-disilane and sym-tetramethyldiphenyldisilane (VIII) with DMSO

A mixture of *sym*-tetramethyldiphenyl-d_{10}-disilane (14 mg, 0.05 mmol), VIII (18 mg, 0.066 mmol), DMSO (9 mg, 0.116 mmol), and dioxane (194 mg, 2.2

mmol) were photolysed as before for 60 min. GLPC analysis as before indicated formation of VII and IX in a ratio of 60 to 40.

The monosilane peak had the following mass spectrum: parent *m/e* 222 (9%), *m/e* 217 (absent), *m/e* 212 (28%), $(P-15)$ *m/e* 207 (37%), *m/e* 202 (absent), *m/e* 197 (100%) indicating the presence of only dimethyldiphenyl-d_{10}-silane (parent 222) and dimethyldiphenylsilane (parent 212).

The disiloxane peak had the following mass spectrum: $(P-15)$ *m/e* 281 (33%), *m/e* 276 (absent), *m/e* 271 (45%), *m/e* 91 (100%), indicating the presence of only *sym*-tetramethyldiphenyl-d_{10}-disiloxane $(P-15, 281)$ and *sym*-tetramethyldiphenyldisiloxane $(P-15, 271)$.

Quantum yield for the disappearance of pentamethylphenyldisilane (I) in the presence of DMSO

A mixture of I (208 mg, 1 mmol), DMSO (78 mg, 1 mmol), cyclododecane (84 mg, 0.5 mmol), and dioxane (1.76 g, 20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated and sealed with a rubber septum.

In a second quartz NMR tube an equal volume of the actinometer solution (made up of n-butyrophenone (396 mg, 2 mmol), cyclododecane (84 mg, 0.5 mmol), and methylcyclohexane added to make a total volume of 10 ml) was taken and the two tubes were placed in a quartz water jacket (26–28°C) at the center of a circular array of sixteen 12″ G.E. Germicidal lamps (2537 Å).

10 μl samples were withdrawn periodically form each tube through the rubber septum and analyzed by GLPC on column A. At the beginning readings were taken every 9 min and towards the end every 30 min. The samples were photolysed for 300 min. The products and starting materials were calibrated against internal standard cyclododecane for varying sensitivities using authentic materials. The disappearance of starting material and appearance of products were plotted against time for both the disilane and the n-butyrophenone actinometer. From the rates of disappearance of n-butyrophenone ($\phi = 0.33$) and the appearance of acetophenone ($\phi = 0.24$) the light intensity (5.61×10^{-8} ein sec^{-1}) was calculated. From the rate of disappearance of I and appearance of II and III, the quantum yields for the disappearance of I (0.56) and appearance of II ($\phi = 0.33$) and III ($\phi = 0.18$) were calculated.

Quantum yield for the disappearance of tetramethyl-1,1-diphenyldisilane (V) in the presence of DMSO

A solution of V as above was photolyzed and analyzed using column B. Quantum yields for the disappearance of V ($\phi = 0.46$) and appearance of II ($\phi = 0.21$) and VI ($\phi = 0.15$) were calculated.

Quantum yield for the disappearance of sym-tetramethyldiphenyldisilane (VIII) in the presence of DMSO

A mixture of VIII as above was photolyzed and analyzed using column B. Quantum yields for the disappearance of VIII ($\phi = 0.52$) and the appearance of VII ($\phi = 0.23$) and IX ($\phi = 0.13$) were calculated.

Acknowledgements

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