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PHOTOLYSIS OF HEPTAMETHYL-2-PHENYLTRISILANE AND OCTAMETHYL-2,3-DIPHENYLTETRASILANE IN THE PRESENCE OF DIMETHYL SULFOXIDE

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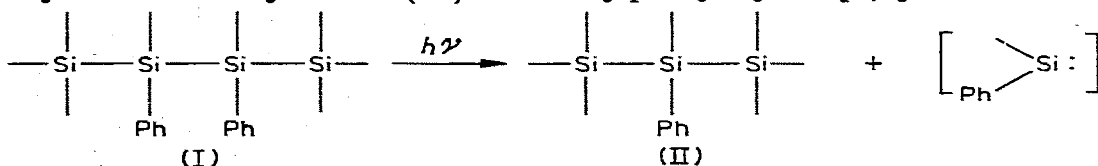
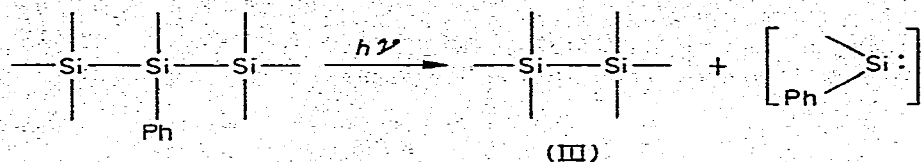
Summary

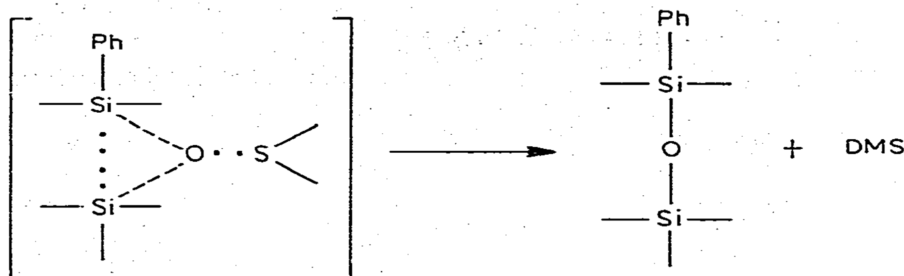
Photolysis of heptamethyl-2-phenyltrisilane and of octamethyl-2,3-diphenyltetrasilane in the presence of dimethyl sulfoxide (DMSO) occurs by two major pathways. The first involves loss of methylphenylsilylene, which reacts with DMSO to yield methylphenylsilanone and dimethyl sulfide. Methylphenylsilanone has been trapped by reaction with hexamethylcyclotrisiloxane (VII) to yield heptamethylphenylcyclotetrasiloxane and by 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (XIII) to yield 1,1,3,5,5-pentamethyl-3-phenyl-2,4-dioxo-1,3,5-trisilacycloheptane. The second pathway involves nucleophilic attack by the oxygen of DMSO on a phenyl substituted silicon atom leading to migration of a phenyl group to an adjacent silicon atom with formation of methyl(trimethylsilyl)silanone and dimethyl sulfide. Methyl(trimethylsilyl)-silanone has been trapped by reaction with VII to yield heptamethyl(trimethylsilyl)cyclotetrasiloxane and by XIII to yield 1,1,3,5,5-pentamethyl-3-trimethylsilyl-2,4-dioxa-1,3,5-trisilacycloheptane. Possible mechanisms for these reactions are considered.

Dimethylsilylene has been shown to deoxygenate dimethyl sulfoxide (DMSO) to yield dimethylsilanone and dimethyl sulfide (DMS) [1]. We were interested whether similar reactivity would be observed with methylphenylsilylene. Photolysis of octamethyl-2,3-diphenyltetrasilane (I) has been shown to yield heptamethyl-2-phenyltrisilane (II) and methylphenylsilylene [2], while photolysis of II yields hexamethyldisilane (III) and methylphenylsilylene [3,4].

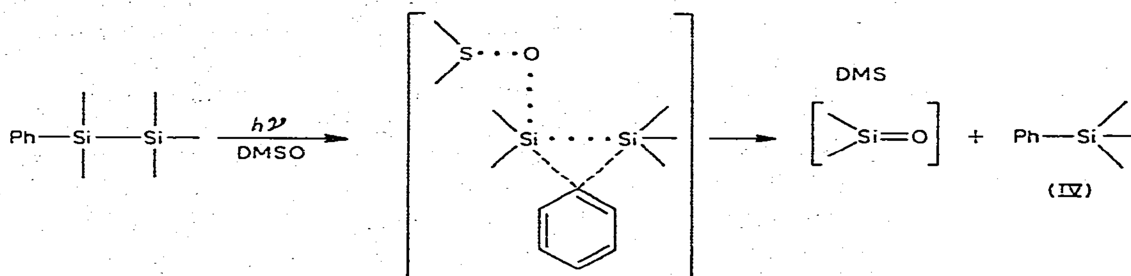




On the other hand, photolysis of aryl-substituted disilanes in the presence of DMSO has been shown to occur by two different pathways [5]. Both appear to involve nucleophilic attack by the oxygen of DMSO on the photoexcited aryl-disilane. The first involves direct attack on the Si—Si single bond to yield an aryl-substituted disiloxane and DMS.



The second may involve 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.



Photolysis of II in the presence of DMSO appears to occur by all three types of processes. Both I and II are stable to DMSO in the absence of light.

For example, photolysis of a deoxygenated solution composed of II (1 mmol), DMSO (1 mmol), and 20 mmol of dioxane for 30 min at 15°C with a 450 W medium pressure Hanovia Hg lamp results in a 76% consumption of II and formation of III (45%), phenyltrimethylsilane (IV) (21%), 1-trimethylsiloxy-1-phenyltetramethyldisilane (V) (8%), 1,1,1,3,5,5,5-heptamethyl-3-phenyltrisiloxane (VI) (2.8%), DMS >95%, and finally, a mixture of methylphenylsilicone oligomers.

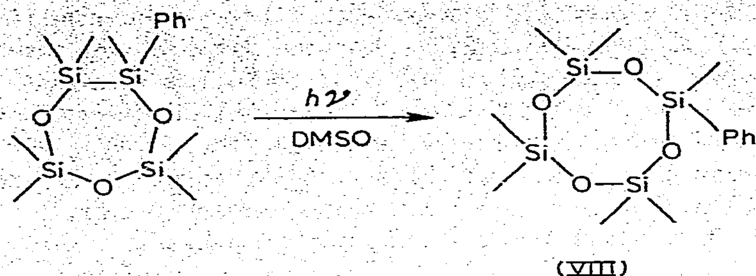
Thus, the major primary photochemical process is the formation of III and methylphenylsilylene which subsequently reacts with DMSO to yield methylphenylsilanone and DMS. In the absence of trapping reagents, methylphenylsilanone oligomerizes. Similar photolysis reactions have been carried out in the presence of hexamethylcyclotrisiloxane (VII, 3 mmol). Dimethylsilanone is known to react with VII to yield octamethylcyclotetrasiloxane [1,6,7]. By

analogy, methylphenylsilanone is expected to react with VII to yield heptamethylphenylcyclotetrasiloxane (VIII). The following results were obtained: recovered II (14%), III (43%), IV (27%), V (5.6%), VI (2.8%), VIII (13%), heptamethyl-(trimethylsilyl)cyclotetrasiloxane (IX) (2.3%), and DMS > 95%. Thus, the trapping efficiency of VII for methylphenylsilanone is about 30%. The recovery of unreacted VII is 92%. Clearly, the presence of VII has not appreciably disturbed the photolysis since the yield of products are virtually unchanged. A major problem is that while VII will trap silanones, it is not very efficient.

(VII) (VIII)

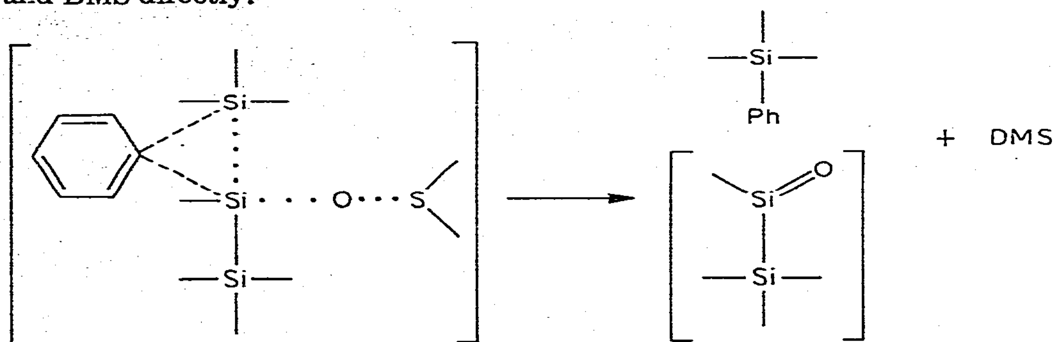
An alternative mechanism for the production of VIII would involve the intermediate formation of 1,2,2,4,4,6,6-heptamethyl-1-phenyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane (X) by insertion of methylphenylsilylene into an Si—O bond of VII. Photochemical oxidation of the aryl-substituted Si—Si single bond of X by DMSO would yield VIII [5]. It should be noted that dimethylsilylene has been shown to insert into the Si—O single bonds of VII to yield the analogous 1,1,2,2,4,4,6,6-octamethyl-3,5,7-trioxa-1,2,4,6-tetrasilacycloheptane [1]. However, control experiments eliminated this possibility. Thus photolysis of I (1 mmol) in the presence of VII (3 mmol) in dioxane (20 mmol) in the absence of DMSO for 20 min results in 55% consumption of I, and formation of II (60%) and III (20%). No X is produced. In addition, there is total recovery (100%) of VII. Apparently, methylphenylsilylene is less reactive than dimethylsilylene as far as insertion into Si—O single bonds of VII is concerned.

(VII) (X)

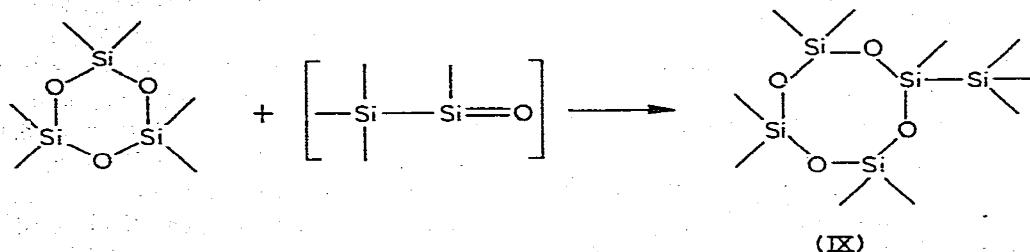


(VIII)

The next most important photochemical process involves nucleophilic attack by the oxygen of DMSO on the aryl-substituted central silicon atom leading to migration of the phenyl group from the central silicon atom to one of the terminal silicon atoms with formation of IV (21%), methyl(trimethylsilyl)silanone, and DMS directly.



Similar photolysis reactions were carried out in the presence of VII (3 mmol) to trap the methyl(trimethylsilyl)silanone intermediate. The expected insertion product IX is isolated in 2.3% yield. Thus the trapping efficiency of VII for methyl(trimethylsilyl)silanone is about 10%.



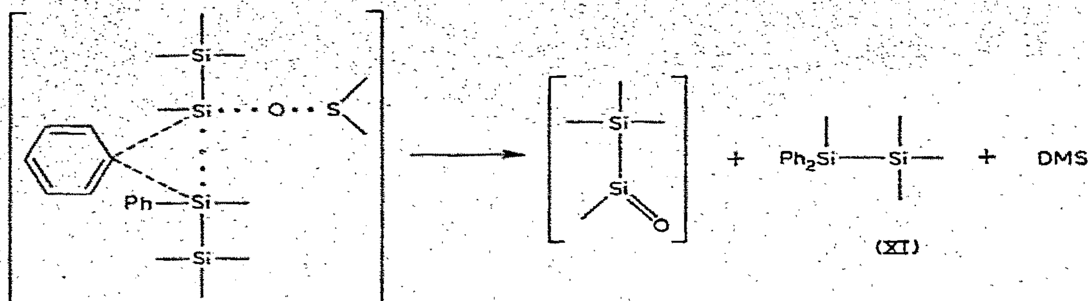
(IX)

The third primary photochemical process involves direct oxidation of the photoexcited Si—Si single bond of II by DMSO to yield V and DMS. This reaction may be related to the direct oxidation of Si—Si single bonds by perbenzoic acid [8—10]. VI is probably formed by direct photo-oxidation of the Si—Si single bond of V by DMSO. It appears to be a secondary photo-product since it is not present early in the photolysis.

Photolysis of I in the presence of DMSO appears to occur initially by the first two of these processes.

For example, photolysis of a deoxygenated solution composed of I 1 mmol, DMSO 1 mmol, and 20 mmol of dioxane for 30 min results in 81% consump-

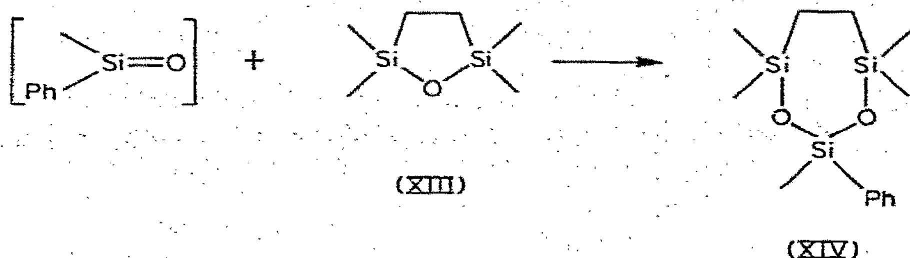
formation of XI, methyl(trimethylsilyl)silanone and DMS directly.



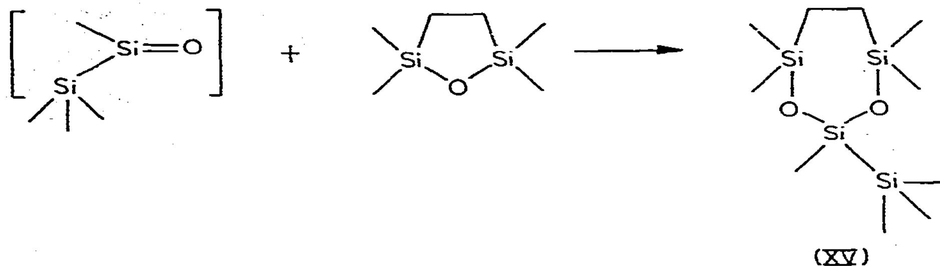
Methyl(trimethylsilyl)silanone is also produced by photolysis of product II with concurrent formation of IV and DMS. The intermediacy of methyl(trimethylsilyl)silanone was established by isolation of IX (6.5%) from the reaction carried out in the presence of added VII. The efficiency for trapping methyl(trimethylsilyl)silanone is 78%. The reason for the high trapping efficiency in this experiment (reproducible with very pure starting materials) is not understood.

A major problem in discussing the photolysis of I is that both the initial photochemical processes lead to products II and XI which can undergo secondary photolysis. The photolysis of II in the presence of DMSO has been previously discussed, while the photolysis of XI in the presence of DMSO has been studied [5]. Thus photolysis of XI in the presence of DMSO yields almost equal amounts of XII, IV, and DMS. The formation of IV is accompanied by the production of methylphenylsilylene which reacts with DMSO to yield methylphenylsilanone and DMS. The amount of IV resulting from this pathway is about 2.2%. On the other hand, the photolysis of II has previously been shown to yield III and IV in a ratio of about 2/1. These results are consistent with the idea that IV is formed principally by these two secondary photolysis pathways.

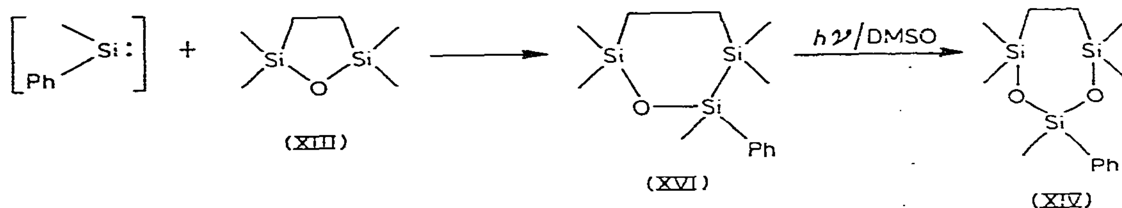
Similar results were obtained when 1,1,3,3-tetramethyl-2-oxa-1,3-disilacyclopentane (XIII) was substituted for VII as a silanone trapping reagent. When a solution composed of I (1 mmol), DMSO (1 mmol), XIII (9 mmol), (a three-fold higher concentration of XIII compared to VII is necessary since XIII has only one reactive Si—O—Si functional group compared to three such groups in VII), in 20 mmol of dioxane was photolyzed, the following products were isolated: recovered I (14%), II (25.5%), III (16%), IV (10.5%), V (2.3%), XI (4.6%), XII (2.3%), 1,1,3,5,5-pentamethyl-3-phenyl-2,4-dioxa-1,3,5-trisilacycloheptane (XIV, 31%), 1,1,3,5,5-pentamethyl-3-trimethylsilyl-2,4-dioxa-1,3,5-trisilacycloheptane (XV, 5.8%), 1,1,2,4,4-pentamethyl-3-oxa-1,2,4-trisilacyclohexane (XVI, 3.5%), and DMS >95%. Unreacted XIII was recovered in approximately 95% yield. The presence of XIII has not disturbed the photolysis since distribution of products: II, III, IV, XI, XII, is similar. The formation of XIV results from insertion of methylphenylsilanone into an Si—O single bond of XIII.



Similarly, the formation of XV results from insertion of methyl(trimethylsilyl)silanone into an Si—O single bond of XIII. Evidently, XIII is not a more efficient silanone trapping reagent than VII.



The formation of product XVI can be accounted for by direct insertion of methylphenylsilylene into the Si—O single bond of XIII [11]. The isolation of XVI permits a direct test of the alternative mechanism we previously ruled out in the reaction of II, VII, and DMSO. Specifically, is XIV formed by photo-oxidation of the phenyl-substituted Si—Si bond of XVI in the presence of DMSO rather than by insertion of methylphenylsilanone into an Si—O single bond of XIII? A control experiment in which pure XVI was photolyzed in the presence of DMSO for 20 min resulted in a 40% recovery of XVI and formation of XIV (21% corrected for recovered XVI). The other products formed from XVI under these conditions are not volatile and have not been determined. Note XIV is stable to these reaction conditions. Since XVI is a minor product (3.5%) from the photolysis of I in the presence of XIII and DMSO, this oxidation pathway makes only a minor contribution to the formation of XIV. The major pathway for the formation of XIV must involve methylphenylsilanone.



Experimental

IR spectra were determined as neat liquids on a Perkin—Elmer 281 instrument. 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 dimethylsulfide 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, Pasadena, California.

Most of the starting materials and products are known compounds. They were prepared following literature methods. They had 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.

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.

Hexamethyldisilane: Silar Laboratories.

1,1,3,3-Tetramethyl-2-oxa-1,3-disilacyclopentane: Silar Laboratories. NMR: 0.13 (s, 12H), 0.72 (s, 4H) ppm.

Trimethylphenylsilane, see ref. 12.

Heptamethyl-2-phenyltrisilane, see ref. 13, 14.

Octamethyl-2,3-diphenyltetrasilane: While this compound has been reported [2], no spectral data have yet appeared. We believe it exists as a mixture of *d,l*- and *meso*-isomers which have not been separated. NMR: δ 0.05 (s, 9H), 0.08 (s, 9H), 0.10 (s, 3H), 0.13 (s, 3H), and 6.93—7.40 (m, 10H) ppm, UV: λ_{max} 2350—2530 Å (flat broad peak), ϵ 7800.

Tetramethyl-1,1-diphenyldisilane: see ref. 15, NMR data ref. 5.

Tetramethyl-1,1-diphenyldisiloxane: see ref. 16, NMR data ref. 5.

1-Trimethylsiloxy-1-phenyltetramethyldisilane: IR (neat): Si—O—Si 1055 cm NMR: δ 0.07 and 0.08 (d, 9H), 0.11 (s, 9H), 0.41 (s, 3H), and 7.21 (m, 5H) ppm Mass spectrum: Parent *m/e* 282, found 282.129, calcd. 282.129, $P-15$, *m/e* 267, found 267.106, calcd. 267.106; $P-73$, *m/e* 209 (100%).

1,1,1,3,5,5,5-Heptamethyl-3-phenyltrisiloxane [17]: IR: Si—O—Si 1060 cm^{-1} NMR: δ 0.12 (s, 18H), 0.23 (s, 3H), 7.04—7.56 (m, 5H).

Heptamethylphenylcyclotetrasiloxane, see refs. 18, 19.

Heptamethyl(trimethylsilyl)cyclotetrasiloxane: IR: Si—O—Si 1075 cm^{-1}. NMR: δ 0.06 (s, 9H), 0.07 (s, 21H) ppm. Mass spectrum: $P-15$, *m/e* 339 (18%), found 339.072, calcd. 339.076; $P-73$, *m/e* 281 (100%), found 281.048 calcd. 281.052.

1,1,3,5,5-Pentamethyl-3-phenyl-2,4-dioxa-1,3,5-trisilacycloheptane: NMR: δ 0.06 (s, 6H), 0.16 (s, 6H), 0.26 (s, 3H), 0.76 (s, 4H), and 7.00—7.50 (m, 5H) ppm. IR (neat): Si—O—Si 1055 cm^{-1}. Mass spectrum: Parent *m/e* 296 (32%), found 296.110, calcd. 296.109; $P-15$, *m/e* 281 (100%).

1,1,3,5,5-Pentamethyl-3-trimethylsilyl-2,4-dioxa-1,3,5-trisilacycloheptane: NMR: δ 0.04 (s, 9H), 0.07 (s, 15H), and 0.70 (s, 4H) ppm IR: Si—O—Si 1050 cm^{-1}. Mass spectrum: Parent *m/e* 292 (16%), found 292.118, calcd. 292.117: $P-15$, *m/e* 277 (23%), found 277.093, calcd. 277.094; $P-73$ *m/e* 219 (100%)

1,1,2,4,4-Pentamethyl-2-phenyl-3-oxo-1,2,4-trisilacyclohexane, see ref. 11.

Dioxane was purified by distillation from lithium aluminiumhydride immediately prior to use.

Dimethyl sulfoxide was stored over Drierite for several days. It was distilled under reduced pressure [20].

Photolysis of heptamethyl-2-phenyltrisilane (II) or octamethyl-2,3-diphenyltetrasilane (I) with DMSO: The following is a typical procedure. A mixture of II 266 mg (1 mmol), DMSO 78 mg (1 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 20 min prior to irradiation with a 450 W medium pressure Hanovia Hg lamp for 20—30 min at 15°C in a water bath. GLPC analysis of the resulting colorless solution on a 1/4" × 30" 20% SE-30 (Column

1) and on a 1/4" × 54" 20% polyphenyl ether (column 2) on Chromosorb P 60/80 mesh showed the formation of III (45%), IV (21%), V (8%), VI (2.8%), and recovered II (24%). Product yields are corrected for recovered starting material. NMR spectra of this mixture indicated formation of DMS in 95% yield. Hexamethyldisilane, IV, V, VI, and recovered II were collected by preparative GLPC on column I after bulb to bulb distillation under reduced pressure (1 mmHg), III, IV, and V were identified by comparison of their IR and NMR spectra and GLPC retention times with those of authentic samples. Compound VI is a new compound and was further characterized by high resolution mass spectra. The residue from bulb to bulb distillation, a viscous liquid, was analyzed by IR and NMR spectra. It was identified as methylphenylsilicone oligomers, on the basis of its IR (Si—O—Si broad peaks at 1080 and 1020 cm^{-1}) and NMR broad peaks at δ 0.17—0.40 and 6.9—7.6 ppm. The reaction of I with DMSO was carried out in a similar manner.

Photolysis of II or I with DMSO and hexamethylcyclotrisiloxane: A mixture of II (266 mg, 1 mmol), DMSO (78 mg, 1 mmol), VII (666 mg, 3 mmol), and dioxane (1.76 g, 20 mmol) was placed in a quartz NMR tube. The solution was deoxygenated and photolyzed as above. The reaction mixture was analyzed by GLPC on Columns 1 and 2. The products were identified by comparison of their IR and NMR spectra and GLPC retention times with authentic samples. IX is a new compound which was further characterized by high resolution mass spectrometry.

Acknowledgements

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