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Preliminary communication

PHOTOLYSIS OF ORGANOPOLYSILANES. REACTIONS OF TRIMETHYLSILYLPHENYLSILYLENE WITH CARBONYL COMPOUNDS

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Summary

Photolysis of tris(trimethylsilyl)phenylsilane (I) in the presence of acetone, diethyl ketone and cyclohexanone resulted in formation of the respective 2,2,2-trimethylphenyldisilanyl enol ethers in moderate yields. UV-irradiation of I in the presence of methyl acrylate, followed by treatment of the reaction mixture with isopropyl alcohol, afforded methyl 3-(1'-isopropoxy-1'-phenyltrimethyldisilanyl)propionate, in addition to an adduct arising from addition of a silicon-carbon double-bonded intermediate to the carbon-carbon double bond.

Recently we have found [1] that trimethylsilylphenylsilylene is produced by photolysis of tris(trimethylsilyl)phenylsilane (I) [2]. In this communication we report concerning the reactions of this silylene with carbonyl compounds.*

When a solution of I (4.19 mmol) and 23.4 mmol of acetone in 100 ml of dry *n*-hexane was irradiated at room temperature for 3 h with a low-pressure mercury lamp bearing a Vycor filter under a nitrogen atmosphere, almost all

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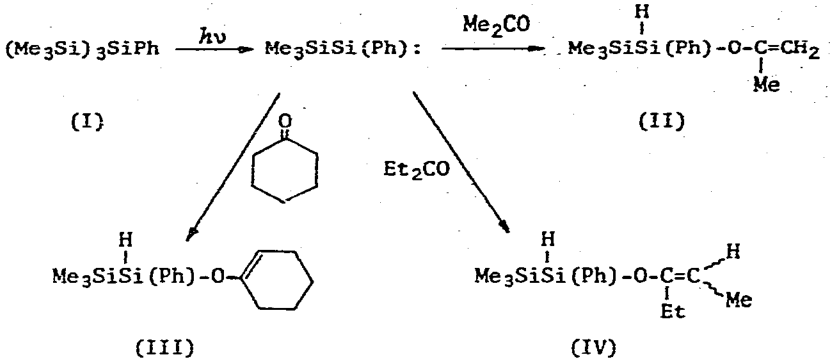
* Recently it has been reported that thermally generated dimethylsilylene reacts with carbonyl compounds to give carbenes and siloxanes [ref. 3].

the starting polysilane was photolyzed, yielding 2,2,2-trimethylphenyldisilanyl enol ether (II) in 33% yield.

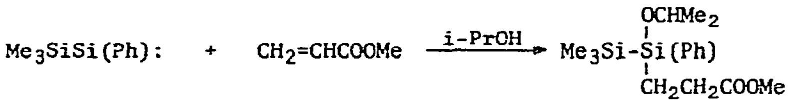
Scheme 1



Compound II could be isolated as a colorless liquid by preparative GLC and its structure was confirmed by mass (m/e 236), IR (cm^{-1}) [ν(Si-H) 2080, ν(Si-O) 1050] and ^1H NMR spectrum (δ) [0.17 (Me_3Si, s, 9H), 1.82 (CH_3-C, broad s, 3H), 3.98, 4.03 (H_2C=C, broad s, 2H), 5.33 (H-Si, s, 1H) and 7.25-7.55 (ring protons, m, 5H)].

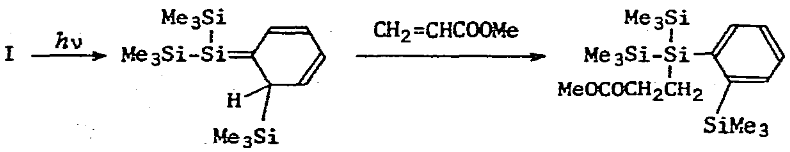
Photolysis of I in the presence of cyclohexanone under similar conditions gave a product identified as disilanyl enol ether (III) [^1H NMR (δ) 0.16 (Me_3Si, s, 9H), 1.50-2.35 (cyclohexenyl ring protons, m, 8H), 4.84 (vinylic proton, broad t, 1H), 5.33 (H-Si, broad s, 1H), 7.20-7.60 (phenyl ring protons, m, 5H); M^+ m/e 276] in 20% yield. Similar photolysis of I with diethyl ketone afforded disilanyl enol ether (IV) in 45% yield. The presence of two doublets of CH_3C=C resonances (at δ 1.52 due to IVa and at 1.54 due to IVb) and two vinyl proton resonances (at δ 4.58 due to IVa and at 4.48 due to IVb) in the ^1H NMR spectrum of IV gave clear indication that both *E*- and *Z*-isomers were present in the ratio of 5/4.

One might consider the possibility that the disilanyl enol ethers II-IV were produced by the reaction of trimethylsilylphenylsilylene with enol forms of the ketones. However, in the reaction of photochemically generated silicon-carbon double-bonded intermediates with enolizable ketones under similar conditions, no products which can be expected from the enol forms of ketones were observed [4]. This fact suggests that the enol forms may be insignificant under the conditions used. Furthermore, the result obtained from the reaction of trimethylsilylphenylsilylene with methyl acrylate strongly indicates that an alternative pathway must be involved in the present system. Thus, irradiation of I (3.25 mmol) with methyl acrylate (19.7 mmol) in 100 ml of dry *n*-hexane gave two volatile products. One of these could only be detected by GLC analysis using a glass column. Attempts to isolate this compound by distillation always led to complete decomposition. However, treatment of the reaction mixture with isopropyl alcohol after irradiation was stopped afforded methyl 3-(1'-isopropoxy-1'-phenyltrimethyldisilanyl)propionate (V) [^{1}H NMR (δ) 0.15 (Me_3Si, s, 9H), 1.19 (Me_2C, d, 6H, J=7.1 Hz), 1.15-1.33 (CH_2-Si, m, 2H), 2.21-2.38 (CH_2-CO, m, 2H), 3.60 (CH_3-O, s, 3H), 4.02 (HC-O, sept., 1H, J=7.1 Hz) and 7.25-7.55 (ring protons, m, 5H); M^+ m/e 324] in 24% yield. The other product (19% yield) was identified as compound (VI) whose formation can be explained in terms of addition of an intermediate (A) [5] to the carbon-carbon double bond of methyl acrylate [^{1}H NMR (δ) 0.17 (Me_3Si, s, 18H), 0.37 (Me_3Si, s, 9H), 1.48-1.66 (CH_2-Si, m, 2H), 2.25-2.42 (CH_2-CO, m, 2H), 3.66 (CH_3-O, s, 3H) and 7.10-7.65 (ring protons, m, 4H); IR (cm^{-1}) ν(C=O) 1745]. This type of reaction has been found in the photolysis of aryldisilanes in the presence of methyl acrylate [4].



$$Me_3SiSi(Ph){:} + CH_2{=}CHCOOMe \xrightarrow{i\text{-}PrOH} Me_3Si\text{-}\underset{CH_2CH_2COOMe}{\overset{OCHMe_2}{Si}}(Ph)$$

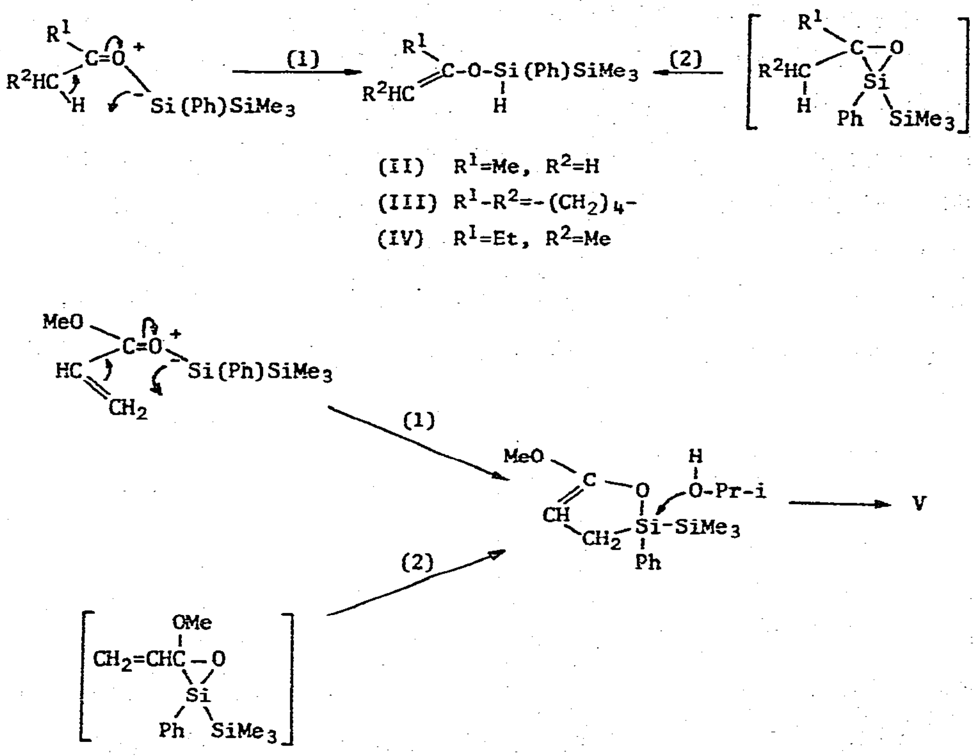
(V)



(A) (VI)

The formation of compounds II-V can be best understood in terms of a concerted pathway (path 1) as shown in Scheme 2. However, a mechanism involving initial formation of a silaoxacyclopropane, followed by isomerization to the observed compounds (path 2), cannot be rigorously excluded at the present time.

Scheme 2



(II) R^1=Me, R^2=H
(III) R^1-R^2=-$(CH_2)_4$-
(IV) R^1=Et, R^2=Me

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