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PHOTOCHEMICAL BEHAVIOR OF 2-PHENYLHEPTAMETHYLTRISILANE IN THE PRESENCE OF ALKENYLTRIMETHYLSILANES

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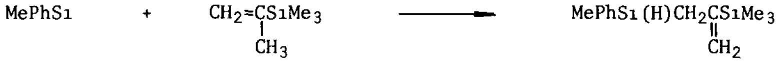
Since our discovery in 1970 of photochemical generation of silylene species from organopolysilanes,[1] much of our work has concentrated on the chemical behavior of various organopolysilanes under photolysis in the presence of diverse substances [2-5] Recently we demonstrated that the diorganosilylene species react with cyclohexene to afford the 3-silylcyclohexene derivatives undoubtedly through initial formation of the silacyclopropane ring, if not isolable, followed by rearrangement [6,7] In this communication we report that the photolysis of 2-phenylheptamethyltrisilane (1) in the presence of either allyl- or isopropenyltrimethylsilane proceeds in line with the mechanism previously presented,[6,7] whereas the photolysis in the presence of vinyltrimethylsilane takes a novel course involving an addition of the silicon-silicon bond across the carbon-carbon double bond

A solution of 1 (4 5 mmol) and 20 g (0 17 mol) of allyltrimethylsilane in 80 ml of dry ethyl ether was irradiated, with ice cooling, for 2 hr with a high pressure mercury immersion lamp bearing a quartz filter Distillation of the reaction mixture gave 1-trimethylsilyl-3-methylphenylsilyl-1-propene (2) in 19% yield as a sole insertion product, together with unchanged 1 (14%) The photolysis of 1 in the presence of isopropenyltrimethylsilane under similar conditions afforded 12% yield of 2-trimethylsilyl-3-methylphenylsilyl-1-propene (3) and a small amount of an unidentified material having a longer retention time on GLC than that of 3 Unchanged 1 (19%) was also recovered

$$\underset{(1)}{\mathrm{Me\ SiMe(Ph)SiSiMe_3}} \xrightarrow{h\nu} \mathrm{MePhSi} + \mathrm{Me_3SiSiMe_3}$$

$MePhSi + CH_2{=}CHCH_2SiMe_3 \longrightarrow MePhSi(H)CH_2CH{=}CHSiMe_3$

(2)



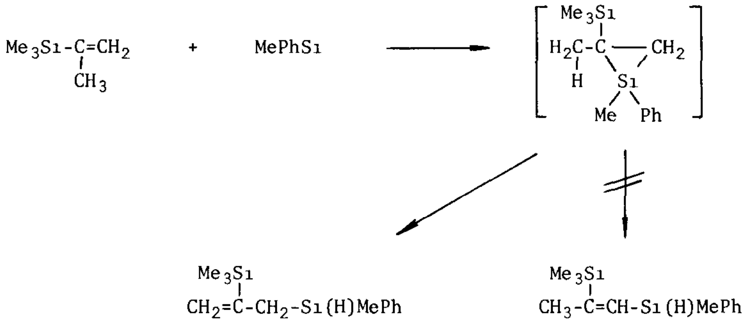
$MePhSi + CH_2{=}\underset{CH_3}{\underset{|}{C}}SiMe_3 \longrightarrow MePhSi(H)CH_2\underset{CH_2}{\underset{\|}{C}}SiMe_3$

(3)

The elemental analyses and IR and mass spectra for the two insertion products, 2 and 3, were completely consistent with the proposed structures The NMR spectrum of 2 showed proton absorptions (τ) at 9 92 (CH_3-$SiMe_2$), 9 73 (CH_3-SiPh), 8 08-8 21 (CH_2-Si), 5 63 (H-Si), 4 60-4 85 (CH=CH), and 2 52-2 83 (C_6H_5-Si), while the spectrum of 3 showed absorptions at 9 98 (CH_3-$SiMe_2$), 9 70 (CH_3-SiPh), 8 17 (CH_2-Si), 5 70 (H-Si), 3 90-5 17 (CH_2=C), and 2 40-2 83 (C_6H_5-Si)

The location of the methylphenylsilyl group in the allylic position was further confirmed by the reaction of 3 with trifluoroacetic acid which gave isopropenyltrimethylsilane in 92% yield [8,9]

The production of both 2 and 3 can be best explained in terms of the transient formation of the respective silacyclopropane derivative, followed by skeletal rearrangement with a 1,3 hydrogen shift from carbon to silicon For example,

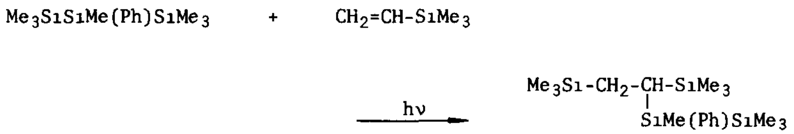


(3) (4)

In both cases, no isomers such as 4, which might be expected to arise from a 1,2 hydrogen shift, were observed *This is of considerable interest in view of the fact that dimethylsilylene* has been reported to react with ethylene in the vapor phase to yield vinyldimethylsilane [10,11]

In an effort to learn whether or not such a 1,2 hydrogen shift could occur under our reaction conditions, *we carried out the photolysis of 1 in the presence of a large excess of tri-*

methylvinylsilane in dry ethyl ether Surprisingly enough, no product that might be expected from the initial addition of methylphenylsilylene into the vinyl system could be observed at all, and a regiospecific double silylation took place 1,2-Bis(trimethylsilyl)-1-tetramethyldisilanylethane (5) was obtained in 14% yield as a sole volatile product, in addition to 12% of the unchanged starting material



$$\mathrm{Me_3SiSiMe(Ph)SiMe_3} \quad + \quad \mathrm{CH_2{=}CH{-}SiMe_3} \xrightarrow{h\nu} \mathrm{Me_3Si{-}CH_2{-}\underset{\substack{|\\ \mathrm{SiMe(Ph)SiMe_3}}}{CH}{-}SiMe_3}$$

(5)

Compound 5 can be shown unambiguously to have the proposed structure by proton NMR spectroscopy Three different resonances of equal intensity from the protons on the three different $\mathrm{Me_3Si}$ groups and a singlet resonance of the MeSi(Ph) group occur at 10 02, 9 93, 9 66 and 9 54 τ, and also multiplet resonances due to the $\mathrm{CH_2}$-CH and Ph-Si groups are found at 9 01-9 34 and 2 43-2 99 τ, respectively The mass spectrum (m/e 366, mol wt calcd 366 82) provided additional support for the structural assignment

The scope and generality of the reaction of the photochemically generated silylene species with other olefins are being examined and will be reported elsewhere

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