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Preliminary communication

PHOTOLYSIS OF ORGANOPOLYSILANES*. EVIDENCE FOR THE FORMATION OF SILACYCLOPROPANE DERIVATIVES AND PHOTO-REARRANGEMENT OF METHYLPHENYLSILACYCLOPROPANE TO AN ISOMERIC OLEFIN

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Summary

Photochemically generated silylene species react with cyclohexene to give silacyclopropane derivatives, which can be quenched with methanol to give the corresponding cyclohexylmethoxysilanes The silacyclopropane system can be stored unchanged in cyclohexane or ether solution, but undergo rearrangement to the 3 silylcyclohexene when further photolyzed

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Although many attempts have been made to prepare silacyclopropanes, all reactions designed to produce this ring system were unsuccesful until 1972, when Lambert and Seyferth reported the preparation of stable silacyclopropanes, viz. 7-siladispiro[2 0 2.1]heptanes [2, 3]. Recently, we reported that the photolysis of 2,3 diphenyloctamethyltetrasilane in the presence of cyclohexene by irradiation with a high pressure mercury lamp bearing a quartz filter leads to the formation of 3-(methylphenylsilyl)cyclohexene, and an intermediate containing a three membered ring system must be formed in this reaction [4].

In this communication we report further evidence for intermediacy of a silacyclopropane derivative in the reaction of photochemically generated silylene species with an olefin.

When 2-phenylheptamethyltrisilane (4.87 mmol) (I) was photolyzed in the presence of 25 g (0.24 mol) of cyclohexene in 150 ml of cyclohexane by irradiation with a low pressure mercury lamp having a Vycor filter for 7 h at ca 45° and the resulting mixture was quenched with 20 ml of dry methyl alcohol. GLC analysis of the mixture showed that 22% yield of cyclohexylmethylphenyl methoxysilane (II) was formed in addition to approximately 3% yield of 3 (methylphenylsilyl)cyclohexene (IV) and a trace of the starting material.

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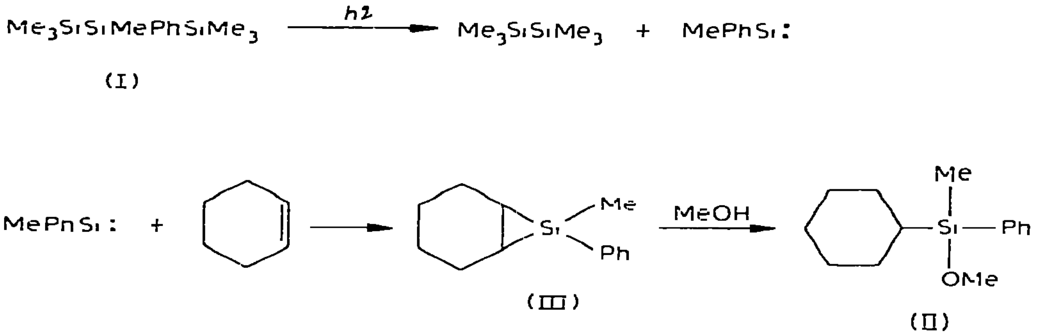
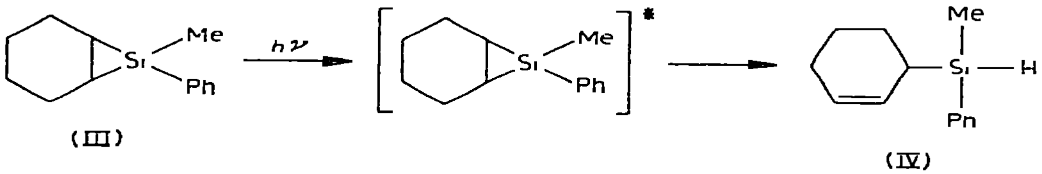
*For related articles see ref 1

Compound II was isolated by preparative GLC. The elemental analysis and NMR (τ) [CH_3Si 9.67; $C_6H_{11}Si$ 8.06-9.18; CH_3OSi 6.58; C_6H_5Si 2 38-2.82] and mass spectroscopic studies (*m/e* 234; mol. wt. calcd. 234.41) were completely consistent with the proposed structure II.

Seyferth et al. have reported that the stable silacyclopropane derivatives react with alcohols very easily to give alkoxysilanes [3]. Therefore our result clearly indicates that 1-methyl-1-phenyl-1 silabicyclo[4.1.0]heptane (III) was formed under the used conditions.



Compound III is quite stable in organic solvents such as cyclohexane and diethyl ether under purified nitrogen atmosphere. For instance, when a cyclohexane solution of III was allowed to stand at room temperature for 24 h and then quenched by methanol, the yield of methoxysilane was not altered. However, attempts to isolate this compound from the reaction mixture were unsuccessful undoubtedly because of its extreme kinetic instability. Nevertheless, the chemistry of III might be investigated in solution without isolation A solution containing III (0.84 mmol)* produced by photolysis of I (3.77 mmol) in the presence of a large excess of cyclohexene in cyclohexane was transferred under a purified nitrogen atmosphere into a reaction vessel equipped with a high pressure mercury lamp with quartz filter and then irradiated for 2 h Interestingly, the photorearranged product IV was obtained in 70% yield at a stage where 82% of III was photolyzed.



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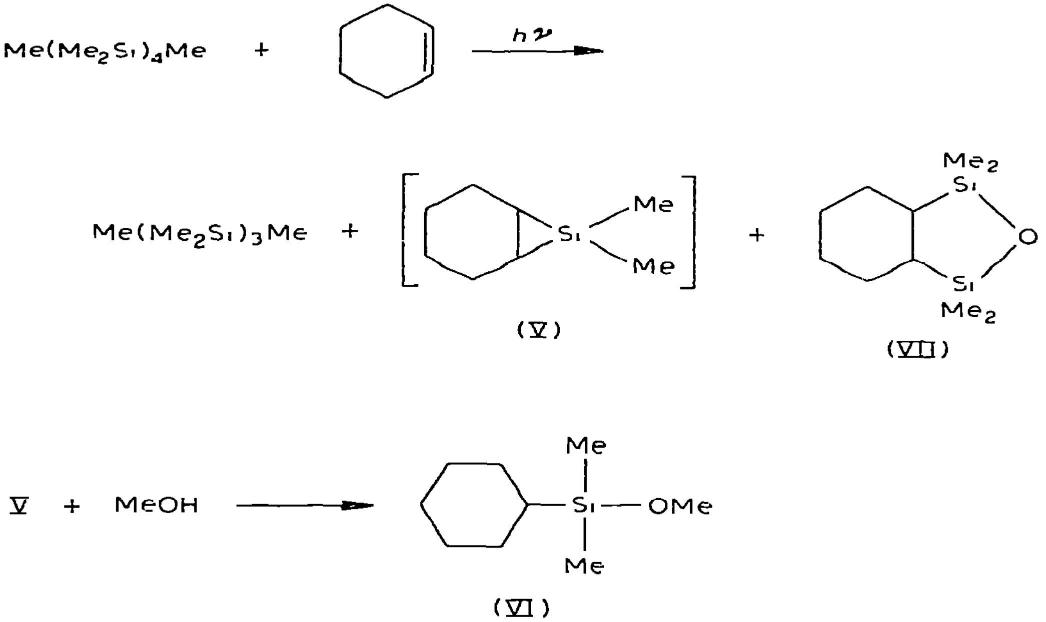
*The amount of III is taken to be equal to the yield of the methoxysilane (II) formed by methanolysis of the photo-product

The present method is not restricted to production of the methylphenyl-substituted silacyclopropane derivative. Thus, the insertion into cyclohexene of dimethylsilylene species generated from decamethyltetrasilane by photolysis, followed by treatment with methyl alcohol gave 6% yield of cyclohexyldimethyl methoxysilane (VI), together with 72% yield of octamethyltrisilane, 2% yield of cyclic siloxane (VII) and a small amount of unidentified products.



Compounds VI and VII were isolated by preparative GLC and identified by NMR (τ) [for VI, CH_3Si 10.03; $C_6H_{11}Si$ 8.10 8.85; CH_3OSi 6.65; for VII, CH_3Si 9.95 and 9.83, $C_6H_{10}Si_2$ 8 30-9 10] and mass spectroscopic studies [for VI, *m/e*. 172; mol. wt. calcd. 172.34; for VII, *m/e*: 214; mol wt. calcd. 214.46].

The formation of VII may be ascribed to accidental oxidation of the disila cyclobutane derivative which would be produced by the insertion of dimethylsilylene species into V [5].

The chemistry of various silacyclopropane derivatives produced from the insertion of the photochemically generated silylene species into many types of olefins is being examined and will be reported elsewhere.

Acknowledgement

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