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Preliminary communication

Photolysis of organopolysilanes. Generation of methylphenylsilylene and its reaction with cyclohexene

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SUMMARY

Photochemically generated methylphenylsilylene reacts with cyclohexene to give 3-(methylphenylsilyl)cyclohexene.

Recently, we have demonstrated that the photolytic generation of silylene species is quite a general reaction for cyclic and acyclic permethylpolysilanes and offers a novel and convenient route to divalent silicon intermediates[1-5]. In this communication we report an insertion of photochemically generated methylphenylsilylene into cyclohexene.

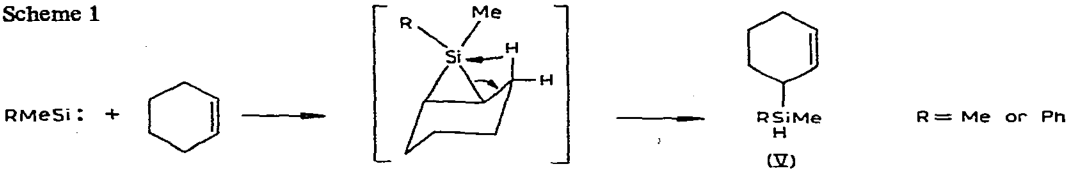
When 2,3-diphenyloctamethyltetrasilane (I)[6] was photolyzed by irradiation with a high pressure mercury lamp in cyclohexane under gaseous nitrogen, methylphenylsilylene was extruded. Thus the photolysis of (I) in the presence of diethylmethylsilane as a trapping agent for 13 h gave two products: 1,1-diethyl-1,2-dimethyl-2-phenyldisilane (II) and 2-phenylheptamethyltrisilane (III)[7,8] in the ratio of 1/1, in addition to some hexamethyldisilane, in high total yield. The formation of hexamethyldisilane indicates that the trisilane (III) underwent further photolysis giving the silylene.

$$\begin{tikzcd}
\underset{\text{(I)}}{Me_3Si(MePhSi)_2SiMe_3} \arrow[r, "h\nu"] & MePhSi: \arrow[d, "Et_2MeSiH"] & + \quad \underset{\text{(III)}}{Me_3SiSiMePhSiMe_3} \\
 & \underset{\text{(II)}}{Et_2MeSiSiMePhH} &
\end{tikzcd}$$

A cyclohexane solution of (I) containing a large excess of cyclohexene was photolyzed under similar conditions for 6 h. In this case, approximately 50% yield of a volatile colorless liquid consisting of 80% of (III) and 20% of 3-(methylphenylsilyl)cyclohexene (IV) was obtained. The elemental analysis and IR [ν(SiH) 2110 cm^{-1}], NMR (τ)

[$CH_3Si(H)Ph$ 9.64 (doublet); ring protons 7.85–8.65; $HSi(Me)Ph$ 5.74 (multiplet); vinyl protons 4.37 (narrow multiplet); $C_6H_5Si(H)Me$ 2.42–2.85] and mass spectra (*m/e* 202; mol.wt. calcd. 202.36) of (IV) were completely consistent with the proposed structure. Moreover, the location of the silyl group in the allylic position was confirmed by the reaction of (IV) with trifluoroacetic acid^{9,10} which gave cyclohexene (70% yield) and cyclohexane (20% yield). The latter is believed to be formed through reduction of the resulting cyclohexene with hydrogen produced by the reaction between the Si–H bond and trifluoroacetic acid. This reduction was proved by an independent experiment. Similarly, when dodecamethylcyclohexasilane$^{11-13}$ was photolyzed in the presence of cyclohexene, 3-(dimethylsilyl)cyclohexene was obtained. The fate of silacyclopropane intermediates, reported to date, is confined only to the production of vinylsilane derivatives$^{14-16}$ or dimerization products^{15,16}. Our results are best explained in terms of the transient formation of the silacyclopropane intermediate, followed by skeletal rearrangement to the isolated compound (V), as shown in scheme 1.

Scheme 1



The insertions of various silylene species into many types of olefines are currently being examined and will be reported elsewhere.

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