Journal of Organometallic Chemistry, 86 (1975) C23–C26

Preliminary communication

PHOTOLYSIS OF ORGANOPOLYSILANES. INSERTION OF SILYLENE SPECIES INTO A CONJUGATED DIENE

MITSUO ISHIKAWA, FUMIO OHI and MAKOTO KUMADA
Department of Synthetic Chemistry, Kyoto University, Kyoto (Japan)
(Received November 5th, 1974, by publisher January 7th, 1975)

Summary

Photolysis of 2-phenylheptamethyltrisilane in the presence of 2,3-dimethylbutadiene afforded several compounds; their formation can be explained by two competitive pathways, the intermediacy of a 2-alkenyl-1-silacyclopropane derivative and a novel addition of the silicon—silicon bond to the conjugated diene.

Recently we have found that when 2-phenylheptamethyltrisilane is photolyzed at 2537 Å in a mixture of cyclohexene and cyclohexane, a silacyclopropane derivative that can be trapped by methyl alcohol is produced [1,2].

In this paper, we wish to report the insertion of photochemically generated silylene species into 2,3-dimethylbutadiene, presenting evidence that the reaction proceeds via a 1,2-addition followed by photorearrangement to acyclic and cyclic olefins, and also a novel photochemical pathway involving a 1,1-addition of the silicon—silicon bond to the terminal unsaturated carbon atom in the butadiene system, with a 1,2-hydrogen shift.

A solution of 2-phenylheptamethyltrisilane (4.85 mmol) and 20 g (0.24 mol) of 2,3-dimethylbutadiene in 80 ml of dry ethyl ether was irradiated, while being cooled in ice, for 2 h with a high pressure mercury lamp bearing a quarz filter. Distillation of the reaction mixture gave three products: 6% yield of 2-(methylphenylsilylmethyl)-3-methylbutadiene (I), 7% yield of 1,3,4-trimethyl-1-phenyl-1-silacyclo-3-pentene (II) and 13% yield of 4-trimethylsilyl-4-tetramethylphenyldisilanyl-2,3-dimethylbutene (III). Unchanged 2-phenylheptamethyltrisilane (8%) was also recovered.

The elemental analyses and IR and mass spectra of the two insertion products, I and II, were completely consistent with the proposed structures. The NMR spectrum of I showed proton absorptions (τ) at 9.71 (CH_3—Si), 8.12 (CH_3C), 7.97 (CH_2—Si), 5.63 (H—Si), 4.99-5.24 (CH_2=C) and 2.50-2.82 (C_6H_5—Si), while the spectrum of II showed absorptions at 9.60 (CH_3—Si), 8.45 (CH_2—Si), 8.27 (CH_3—C) and 2.65-3.04 (C_6H_5—Si).

The present findings, especially the formation of I which can best be explained by skeletal rearrangement of the 1,2-adduct A, were of considerable interest to us because, to our knowledge, most, if not all, of the reactions of silylene species with 1,3-butadiene derivatives reported to date are concerned with the formation of silacyclopentenes [3—9], although these apparent 1,4-addition products have been assumed to be formed via a 1,2-addition, followed by rearrangement. No evidence to support the formation of such 1,2-adducts, however, has been presented so far.

In order to trap the 1,2-adduct, we photolyzed 2-phenylheptamethyltrisilane (4.71 mmol) by irradiation with a low pressure mercury lamp (2537 Å) at 0° for 6 h under bubbling nitrogen, in the presence of 20 g (0.24 mol) of 2,3-dimethylbutadiene in 150 ml of dry ethyl ether. After the irradiation was stopped, a dropping funnel was installed between the reaction vessel and the nitrogen gas out-let tube, from which 20 ml of dry methyl alcohol was added dropwise to the reaction mixture over a period of 20 min at 0°. Distillation gave 6% yield of 2,3-dimethyl-4-(methylphenylmethoxysilyl)-2-butene (IV), in addition to I (6%), II (7%), III (23%) and the recovered trisilane (16%).

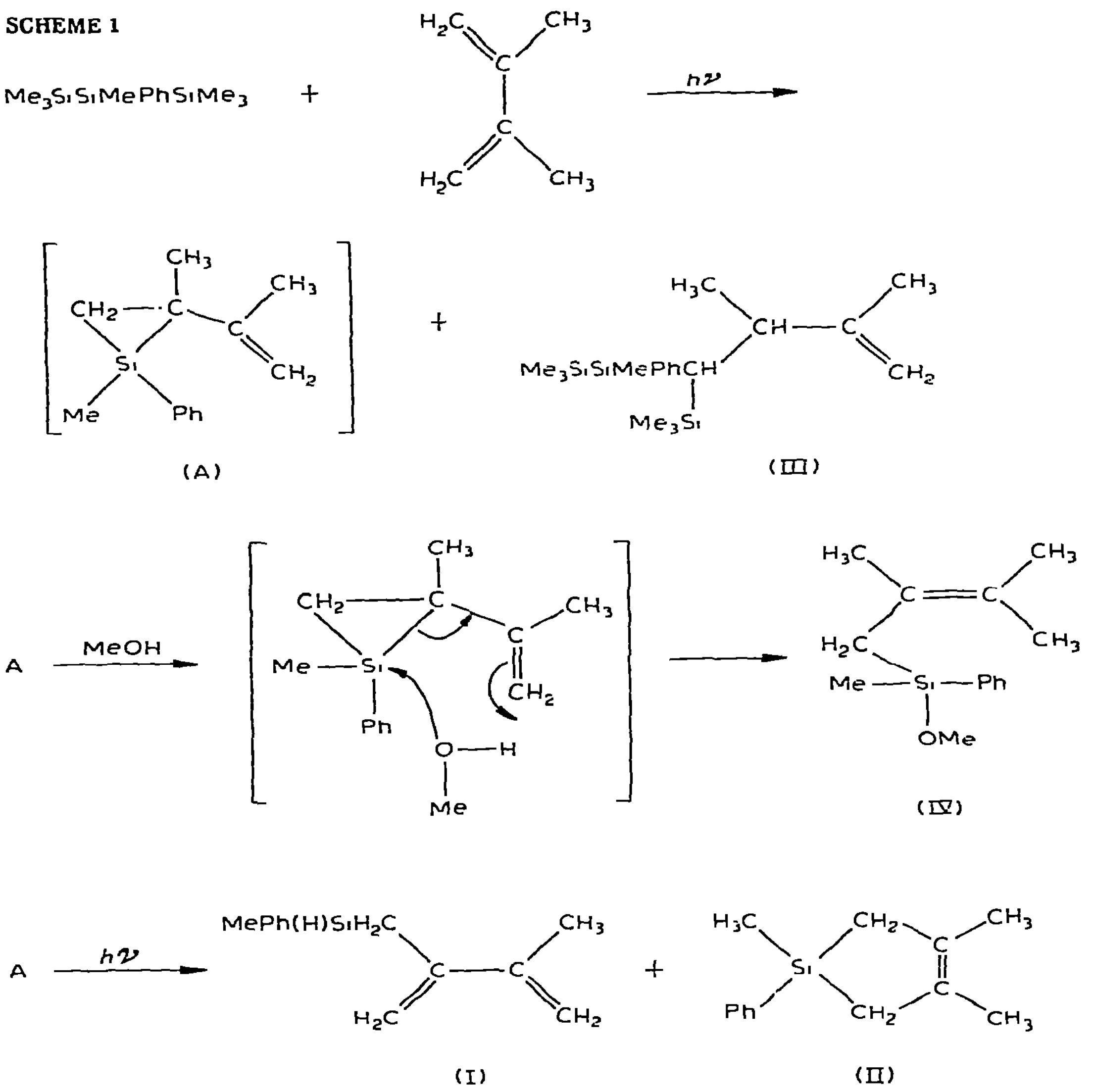
The proton NMR spectrum of IV showed five singlet peaks at τ 9.67, 8.53, 8.47, 8.26 and 6.57 with relative intensities 3/3/6/2/3 attributed to CH_3—Si, CH_3—C, $(CH_3)_2C$, CH_2—Si and CH_3—O protons, respectively, as well as a complex pattern due to the phenyl ring protons at τ 2.90-2.37. The mass spectrum (*m/e* 234; mol wt. calcd. 234.42) was also consistent with the proposed structure. Since compound II did not react with methyl alcohol under the conditions used, compound IV must come from the 1,2-adduct.

From these observations we believe that the insertion of silylene species into the diene system proceeds through a 1,2-addition, and the resultant 2-alkenyl-1-silacyclopropane derivative rearranges to give both the butadiene derivative I and silacyclopentene II as shown in Scheme 1.

However, it is difficult, at present, to rule out the possibility that compound II also comes from a direct 1,4-addition process.

The production of III can be explained by a novel photochemical 1,1-addition of a silicon—silicon bond to the terminal unsaturated carbon atom with a 1,2-hydrogen shift. The isolated III is gas-chromatographically homogeneous under several conditions, and its mass spectrum showed a parent peak at 348, corresponding to the calculated molecular weight for $C_{19}H_{36}Si_3$. However, the 100 MHz proton NMR and proton-decoupled NMR spectra of III showed the presence of at least two kinds of diastereoisomers in the ratio of approximately 2/1. The abundant species exhibited proton absorptions (τ) at 9.91 (CH_3—$SiMe_2$), 9.65 (CH_3Si—Si), 9.47 (CH_3SiPh), 9.13 (CH_3—CH, $J = 6.8$ cps), 8.96 (HC—CHSi, $J = 6.6$ cps), 8.37 (CH_3—C), 7.69 (HC—Me, centre of multiplet), 5.47 ($H_2C{=}C$) and 2.39-2.94 (C_6H_5—Si), while the spectrum of the other showed 9.94 (CH_3—$SiMe_2$), 9.65 (CH_3Si—Si), 9.47 (CH_3—SiPh), 9.17 (CH_3CH, $J = 6.8$ cps), 8.85 (HC—CHSi, $J = 5.3$ cps), 8.37 (CH_3—C), 7.69 (HC—Me, centre of multiplet), 5.40 ($CH_2{=}C$) and 2.39-2.94 (C_6H_5—Si). Irradiation of a multiplet signal at τ 7.69 changed two doublets at τ 9.17 and 9.13 into a broad singlet, and two doublets at τ 8.96 and 8.85 into two singlets. These results are completely consistent with the proposed structure for III.

SCHEME 1



The photolysis of various polysilanes in the presence of many types of conjugated dienes are currently being examined and will be reported elsewhere.

Acknowledgement

The cost of this research was defrayed in part by a Grant-in-Aid for Scientific Research by the Ministry of Education, to which the authors' thanks are due.

References

1 M. Ishikawa, M. Ishiguro and M. Kumada, J. Organometal. Chem., 49 (1973) C71.
2 M. Ishikawa and M. Kumada, J. Organometal. Chem., 81 (1974) C3.
3 W.H. Atwell and D.R. Weyenberg, J. Amer. Chem. Soc., 90 (1968) 3438.
4 Y.N. Tang, G.P. Gennaro and Y.Y. Su, J. Amer. Chem. Soc., 94 (1972) 4355.
5 G.P. Gennaro, Y.Y. Su, O.F. Zeck, S.H. Daniel and Y.N. Tang, Chem. Commun., (1973) 637.
6 R. Maruca, J. Org. Chem., 36 (1971) 1626.
7 H. Okinoshima, K. Yamamoto and M. Kumada, J. Amer. Chem. Soc., 94 (1972) 9263.
8 O.F. Zeck, Y.Y. Su, G.P. Gennaro and Y.N. Tang, J. Amer. Chem. Soc., 96 (1974) 5967.
9 P.P. Gaspar and R.J. Hwang, J. Amer. Chem. Soc., 96 (1974) 6198.