[$PdCl_2(PEt_3)_2$]-Catalysed Formation of 1,4-Disilacyclohexa-2,5-diene from 1-Silacyclopropene

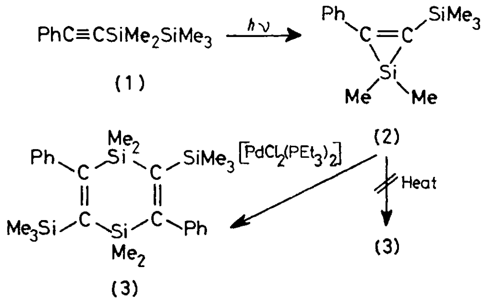
By Mitsuo Ishikawa,* Takamasa Fuchikami, and Makoto Kumada*

(*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto* 606, *Japan*)

Summary Photolysis of phenylpentamethyldisilanylacetylene in the presence of [$PdCl_2(PEt_3)_2$] afforded 1,1,4,4-tetramethyl-2,5-bis(trimethylsilyl)-3,6-diphenyl-1,4-disilacyclohexa-2,5-diene *via* dimerization of an initially formed 1-silacyclopropene.

It is well known that the dimethylsilylene species generated by thermolysis reacts with substituted acetylenes yielding 1,4-disilacyclohexa-2,5-dienes.[1] To account for the formation of such compounds, Barton and Kilgour have recently proposed a mechanism involving a Diels–Alder addition of an acetylene to a 1,4-disilabuta-1,3-diene arising from ring opening of a 3,4-disilacyclobutene[2] (not dimerization of the silacyclopropene). Here we report the first example of the formation of a 1,4-disilacyclohexa-2,5-diene *via* dimerization of a silacyclopropene in the presence of [$PdCl_2(PEt_3)_2$] as catalyst.

Recently we have reported that photolysis of phenylpentamethyldisilanylacetylene (**1**) affords 1,1-dimethyl-2-trimethylsilyl-3-phenyl-1-silacyclopropene (**2**) in solution.[3] Now we have found that compound (**2**) readily undergoes dimerization with high stereoselectivity by the catalytic action of [$PdCl_2(PEt_3)_2$] at 60 °C in benzene. Thus, when a solution of (**1**) (2·42 mmol) in the presence of [$PdCl_2(PEt_3)_2$] ($1{\cdot}2 \times 10^{-2}$ mmol) in 80 ml of dry benzene was irradiated at 60 °C for 3 h with a low-pressure mercury lamp under N_2, almost all the starting disilane (**1**) was photolysed to give the disilacyclohexadiene (**3**) as white crystals (m.p. 163—165 °C), in 67% yield, in addition to trimethylsilylphenylacetylene (12%) and a compound (10%) whose mass spectrum showed M^+ at *m/e* 522·2419, corresponding to the calculated molecular weight $C_{28}H_{46}Si_5$. Interestingly, no other isomers of (**3**) were detected by either g.l.c. or spectroscopic analysis. Control experiments proved that this reaction did not occur in the dark at 80 °C.



The structure of (**3**) was confirmed by its ^1H n.m.r. spectrum [δ −0·25 (Me–SiMe$_2$, s, 18H), 0·12 (Me–SiMe, s, 12H), and 6·8–7·3 (ring protons, m, 10H)] and its exact parent peak (found, *m/e* 464·2254; calc. *m/e* 464·2207).

This pathway is substantiated by the following separate experiments. A solution containing (**2**) (1·2 mmol) was prepared by photolysis of (**1**) (2·36 mmol) in 80 ml of dry benzene. Heating this solution in the absence of catalyst at 60 °C for 4·5 h under N_2 resulted in no change of the silacyclopropene (**2**), thus indicating that a thermal process is not responsible for the dimerization of (**2**). By contrast, treatment of the same solution as above with $1{\cdot}2 \times 10^{-2}$ mmol of [$PdCl_2(PEt_3)_2$] at 60 °C for 4·5 h gave compound (**3**) in 75% yield, [based on unrecovered (**2**)] as the sole product.[4]

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[1] M. E. Vol'pin, Y. D. Koreshov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, 1962, **18**, 17; W. H. Atwell and D. R. Weyenberg, *Angew. Chem. Internat. Edn.*, 1969, **8**, 469.

[2] T. J. Barton and J. A. Kilgour, *J. Amer. Chem. Soc.*, 1976, **98**, 7746.

[3] M. Ishikawa, T. Fuchikami, and M. Kumada, *J. Amer. Chem. Soc.*, 1977, **99**, 245.

[4] Recently, Seyferth *et al.* have reported that the reaction of a silacyclopropene with [$PdCl_2(PPh_3)_2$] in the presence of phenylacetylene gives a silacyclopentadiene: D. Seyferth, D. P. Duncan, and S. C. Vick, *J. Organometallic Chem.*, 1977, **125**, C5.