

Synthesis of 1,1-Dichloro-2,3,4,5-Tetraphenyl-1-Silacyclopenta-2,4-diene and Its Reaction with Alkali Metal: Evidence for the Formation of Silylanion

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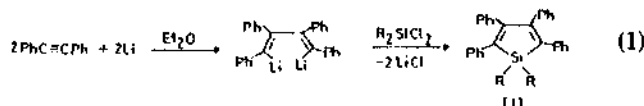
1,1-Dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was synthesized through the reaction of SiCl_4 with 1,4-dithio-tetraphenylbutadiene in 50% yield. From the reaction of this silole with metal, an air sensitive red-brownish solid was obtained. Treatment of this reaction product with CH_3I and Me_3SiCl gave 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene and 1,1-bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene, respectively. From these results, the formation of reactive 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-dienyl dianion was confirmed.

Introduction

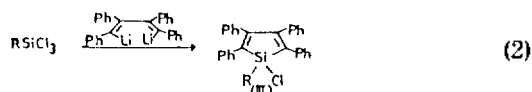
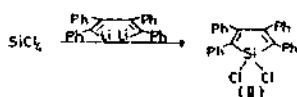
The chemistry of 1-silacyclopenta-2,4-diene is of much interest over past decade as an analogy of cyclopentadiene.¹⁻⁴ Especially, the functionally substituted 1-silacyclopenta-2,4-diene is much more attractive species because it might serve as a source of five membered ring with 6π -electrons in the form of silyl-anion or silylene.⁵⁻⁷ Therefore, it might be expected that from the reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene with alkaline metal in a suitable solvent the corresponding silyl anion or silylene could be obtained, because the four phenyls in 2,3,4,5-positions would influence for the delocalization of silyl anion into 6π -electron system and stabilize the silyl anion or silylene. In an attempt to investigate such a probably stable silyl anion or silylene, we have synthesized 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene and studied the reaction with alkali metal.

Results and Discussion

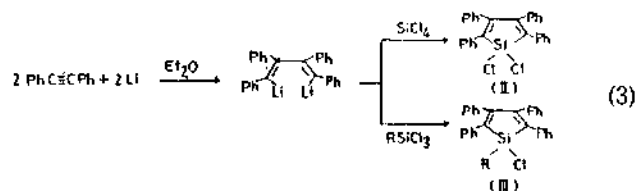
Although 1-silacyclopenta-2,4-diene is an attractive species, the synthetic routes to such functionally substituted compounds are rather limited.⁸⁻¹⁰ In general, 1,1-diorgano-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was prepared when diorganodihalosilane was added to a suspension of 1,4-dithio-tetraphenylbutadiene in ether as shown in equation (1)



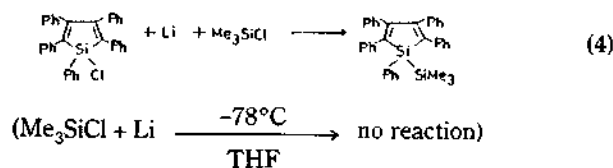
It was reported that this procedure (1) was unsuccessful in the synthesis of functionally halosubstituted 1-silacyclopenta-2,4-diene, but successful only when 1,4-dithio-tetraphenylbutadiene was added dropwise to RSiCl_3 or SiCl_4 solution as shown in equation (2)¹¹⁻¹²



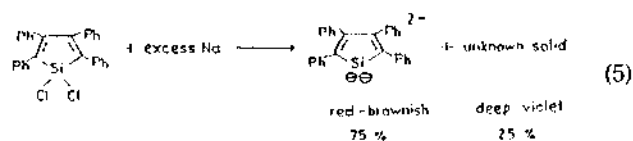
From our experience this reaction procedure (2) seems to be unusual, because dilithio-dianion is in general very reactive and slightly soluble in organic solvent. Consequently, we succeeded in synthesizing the functionally substituted 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene in a good yield by the generally applied procedure (1) as shown in equation (3). In this reaction a little amount of octaphenyl-1,1-bissilole was also isolated.



It was well known that the formation of silyl anion in solution from the corresponding silylhalide with alkali metal was also limited.^{13,14} Recently it was reported that the silyl anion was formed as shown in equation (4).¹²



Our study focussed on the preparation of silyl anion and/or silylene from the reaction of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene with alkali metal in dioxane. From this reaction we have succeeded in isolating quantitatively red-brownish 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-dienyldianion, which was insoluble in dioxane, but to some extent soluble in THF, and a little amount of deep violet solid, which was soluble in dioxane but yet not identified.



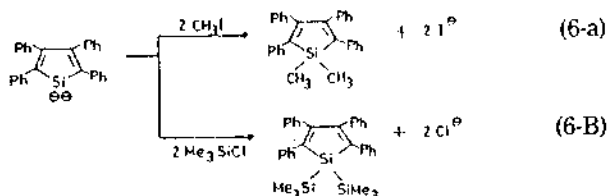
This reaction was favoured by alkali metal in the order $\text{K} > \text{Na} > \text{Li}$ in terms of reaction time and in solvent having high boiling point. This relationship was given in Table 1.

Table 1. The Influence of Metal and Solvent

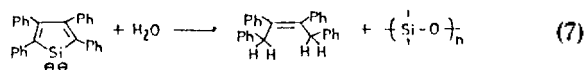
Solvent	Dioxane			n-Octane			n-Heptane			Benzene		
b.p. °C	101.1			125.6			98.4			80.1		
Metal	K	Na	Li	K	Na	Li	K	Na	Li	K	Na	Li
Reaction ^a time, hrs	0.5	2	-	0.5	5	-	3	36	-	-	-	-

^adefined when the deep violet color appeared in solutions.

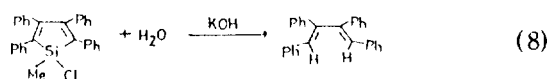
The red-brownish silyl dianion was so sensitive that it was flammable immediately in the air. The reaction of this silyl dianion with CH_3I and Me_3SiCl gave the expected 1,1-dimethyl- and 1,1-bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene, respectively.



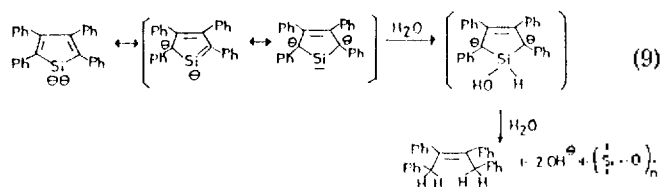
Quenching this silyl dianion with H_2O gave the decomposed product of 1,2,3,4-tetraphenylbutene-2 together with $(\text{Si-O})_n$ polymer.



It was known that 1-methyl-1-chloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was also decomposed in strong alkaline medium to 1,2,3,4-tetraphenylbutadiene as shown in equation (8).¹¹



Therefore, it was quite reasonable that 1,2,3,4-tetraphenylbutene-2 was obtained from the readily reduced 1-silacyclopenta-2,4-dienyl dianion. We would like to propose this reaction pathway as following.



Experiments

All of the reactions and treatments were proceeded under

nitrogen atmosphere by using vacuum line. Ir spectra were obtained on Shimadzu 440, nmr on BRUKER WP80 SY, 80MHz and mass spectra on Jeol Gas Chromatography and Mass Spectrometer DMX 300. Elemental Analysis was obtained from the Dept. of Chemical Engineering, Seoul National University.

1,4-Dilithiotetraphenylbutadiene: This compound was prepared according to the procedure of Gilman.²

1,1-Dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene A 120ml diethylether suspension of 1,4-dilithiotetraphenylbutadiene obtained from 10.7g (60 mmoles) of diphenylacetylene and 0.5g (71 mg atoms) of lithium was frozen by using liquid nitrogen followed by adding 8.0 ml (70 mmoles) of SiCl_4 under nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature with stirring (about 2-3 hrs.) and then the greenish-yellow solution was separated from the precipitate by decantation. This treatment was done two or three times by adding each 150 ml of ether. After about a half of the solvent of the greenish-yellow solution was evaporated, the solution was kept at -78°C for one day. A greenish-yellow crystal of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was obtained. Yield: 7.6g (50%), m.p. = 195°C (Lit: 197°C), Anal. calcd. for $\text{C}_{28}\text{H}_{20}\text{Cl}_2\text{Si}$, C = 73.84%, H = 4.43%, found, C = 74.44%, H = 4.44%, ir: ν_{SiCl} = 571 cm^{-1} (vs) and 538 cm^{-1} (vs), mass: m/e = 455, 457 and 459 corresponding to the isotopes of 35 and 37 of Cl. The residue was extracted with ether and the extract was kept at -78°C for several days. A yellow crystal of octaphenyl-1,1'-bissilole was obtained. Yield: 0.8g (5%), m.p. = 260°C , Anal. calcd. for $\text{C}_{56}\text{H}_{40}\text{Si}$, C = 90.77%, H = 5.44%, found, C = 88.08%, H = 5.14%, mass: m/e = 741

1,1-Disodio-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (Silyl-dianion) 0.6g (26mg atoms) of sodium was added under nitrogen atmosphere to a dioxane solution (30 ml) of 2.28g (5 mmoles) of 1,1-dichloro-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene. When this reaction mixture was refluxed for two hours, the greenish-yellow color of the solution changed to deep violet and at the same time solid was precipitated. Reflux was continued under stirring for additional 5 hours. After filtering, followed by extraction of the precipitate with THF, 1.6g of red-brownish solid, 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was obtained. From the residue, 9.70mmoles of NaCl and an unreacted sodium metal were found. From the filtrate, the solvent of dioxane was evaporated and 0.5g of deep violet, yet unidentified solid was obtained. When this reaction was performed in an identical manner with Li and K in n-octane, n-heptane and benzene, it was observed that Li did not react and K reacted most rapidly. These relationship was summarized in Table 1.

1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene 1.88g of red-brownish 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene (silyl-dianion) was contacted with vapour of CH_3I for 1 hour in vacuum line. The red-brownish color of the silyl-dianion changed to yellow. After adding 10ml pentane to the yellow solid, the solution was kept at -20°C for one day. A greenish-yellow crystal of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was obtained quantitatively. Yield: 1.63g (93%), m.p. = $160-162^\circ\text{C}$, Anal. calcd. for $\text{C}_{30}\text{H}_{26}\text{Si}$, C = 86.91%, H = 6.32%, found C = 85.70%, H = 6.24%, mass: m/e = 414, $^1\text{H-nmr}$ (CDCl_3): δ = 6.7-7.2 ppm(brd.m, 20H- C_6H_5), 0.46 ppm(s,

6H-CH₃), ir: $\nu_{\text{ar-H}} = 3050 \text{ cm}^{-1}$ (m), $\nu_{\text{al-H}} = 2990 \text{ cm}^{-1}$ (m), $\nu_{\text{Si-CH}_3} = 1260 \text{ cm}^{-1}$ (vs).

1,1-Bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene The reaction of 2.10g of red-brownish 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene(silyl-dianion) with vapour of Me₃SiCl was proceeded in vacuum line for two hours in an identical manner as described above. The red-brownish color of the silyl-dianion changed to yellow. After crystallization from methanol a greenish-yellow crystal of 1,1-bis(trimethylsilyl)-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene was obtained quantitatively. Yield: 2.41g (95%), m.p. = 99-100°C, Anal. calcd. for C₃₄H₃₈Si₃, C = 76.92%, H = 7.23%, found C = 76.87%, H = 7.21%, mass, m/e = 531, ¹H-nmr(CDCl₃), 6.7-7.2 ppm (brd.m, 20H-C₆H₅), 0.1 ppm(s, 18H-CH₃), ir, $\nu_{\text{ar-H}} = 3050 \text{ cm}^{-1}$ (m), $\nu_{\text{al-H}} = 2950 \text{ cm}^{-1}$ (m), $\nu_{\text{Si-CH}_3} = 1245 \text{ cm}^{-1}$ (vs).

Quenching 1,1-disodio-2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene with H₂O 1.22g of the red-brownish silyl-dianion was contacted with vapour of H₂O in vacuum line for 30 minutes. The red-brownish color changed to pale yellow immediately. After adding 30 ml of ether to this pale-yellow solid, the ether solution thus obtained was filtered and kept at -20°C for one day. A colorless crystal of 1,2,3,4-tetraphenylbutene-2 was obtained. Yield: 0.67g (71%), m.p. = 62°C, Anal. calcd. for C₂₈H₂₄, C = 93.29%, H = 6.66%, found C = 93.26%, H = 6.42%, mass, m/e = 360, ¹H-nmr(CDCl₃), 6.95-7.21 ppm(brd.m, 20H-6₆H₅), 4.02 ppm(s, 4H-CH₂) ir, $\nu_{\text{ar-H}} = 3030 \text{ cm}^{-1}$ and $\nu_{\text{ar-H}} = 2960 \text{ cm}^{-1}$ (m). The residue was colorless and did not melt above 360°C. In ir only Si-O vibration was observed at 1020 cm⁻¹ (vs).

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New Polyacetylene Compounds from Panax Ginseng C.A. Meyer†

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Two polyacetylene compounds having diyn-ene chromophore were isolated from fresh Korean ginseng roots through solvent fractionation, partition and silica gel column chromatography. The low pressure semi-preparative liquid chromatography and high performance preparative liquid chromatography were used for final separation of polyacetylenic fractions. The chemical structures of these polyacetylenes were determined to be heptadeca-1,8-dien-4,6-diyn-3,10-diol and heptadeca-1,4-dien-6,8-diyn-3,10-diol by UV, FT-IR, ¹H NMR, ¹³C NMR, mass spectra and elemental analysis.

Introduction

Panax ginseng C. A. Meyer belongs to the Araliaceae family and has been known for many years as the most valued medicine having mysterious effects among all the herbal medicines and plants in Korea, China and Japan.

† Dedicated to Professor Sae-Hee Chang occasion of his 60th birthday.

The polyacetylene compound from ginseng roots was first obtained by Takahashi *et al.* as a yellowish viscous liquid through distillation and silicic acid column chromatography of the ether soluble neutral portion.^{1,2} The structure was turned out to be identical with falcarinol isolated from *Falcaria Vulgaris* B.³ and carotatoxin isolated from *Daucus carota* L..⁴ Wrobel *et al.* also isolated other C₁₇ polyacetylene compounds from ginseng.⁵⁻⁷