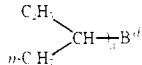
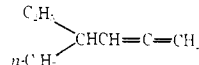

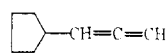

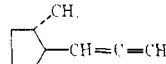

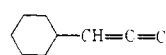


adjacent carbon concomitant with an electron pair shift and loss of chloride.

Protonolysis of the allenic borane **2** at 25–30° with acetic acid afforded, after work-up, a 75% isolated yield of cyclopentylallene. However, it should be noted that the allene contained a small amount of methylcyclopentylacetylene (~3%). In exploring the full scope of this novel allene synthesis using acetic acid in the protonolysis step, it was observed that the amount of methylalkylacetylene formed increased markedly when the temperature during the preparation of the lithium chloropropargylide and the ate complex **1** were allowed to rise above –60°. We are currently investigating the nature of the precursor which leads to methylalkylacetylenes.

In order to determine the stereochemistry of the migrating group, tri(2-*trans*-methylcyclopentyl)borane was treated with the lithium chloropropargylide. Acetolysis of the reaction mixture afforded 1-(*trans*-2-methylcyclopentyl)-1,2-propadiene,⁷ indicating that the migration of the 2-methylcyclopentyl moiety must have proceeded with retention of configuration. A summary of the experimental results obtained for the synthesis of various allenes is given in Table I.

Table I. Yields of Allenes Obtained *via* the Reaction of Lithium Chloropropargylide with Various Trialkylboranes

Trialkylborane	Product allene ^{a,b}	Isolated yield, %
$(n\text{-C}_6\text{H}_{13})_3\text{B}$	$n\text{-C}_6\text{H}_{13}\text{CH}=\text{C}=\text{CH}_2$	73 ^c
		74
		75
		76
		77

^a The nmr, ir, and mass spectral data for all new compounds reported are consistent with the structures proposed. ^b The allene products were better than 95% pure. ^c Glpc analysis revealed that the 1,2-nonadiene contained approximately 7% of the isomeric allene resulting from the reaction of lithium chloropropargylide with the organoborane derived from addition of BH_3 to the 2 position of 1-hexene. ^d Derived from hydroboration of *trans*-3-hexene.

The following description of the preparation of 1-cyclohexyl-1,2-propadiene is representative. To a solution of cyclohexene (60 mmol) in THF (10 ml) was added a 2 M solution of borane (20 mmol) at such a rate as to maintain the temperature at 25–45°. The reaction mixture was stirred at 40–45° for an additional 3 hr before being added to the lithium chloropropargylide.

Propargyl chloride (20 mmol) in THF (10 ml) was placed into a separate flask. The solution was cooled to –70°, then diluted with a 1.6 M solution of methyl-lithium (20 mmol) in ether while maintaining the temperature during the addition between –70 and –60°. To the resultant lithium chloropropargylide was added immediately the solution of tricyclohexylborane, keep-

(7) The stereochemistry of the allene follows from its hydrogenation to *trans*-1-methyl-2-propylcyclopentane.

ing the temperature during the addition between –70 and –60°. The reaction mixture was allowed to warm up to room temperature, the THF and ether were removed under reduced pressure, and the residue obtained was diluted with 5 ml of acetic acid. The mixture was stirred at 25–30° for 1 hr and the allene formed was distilled under reduced pressure into a receiver immersed into a Dry Ice–acetone bath. The distillate was neutralized with aqueous sodium hydroxide to remove acetic acid, and the allene was extracted with pentane. After drying with magnesium sulfate, the pentane was removed and the residue was distilled to give 1.9 g (77%) of 1-cyclohexyl-1,2-propadiene; bp 58° (12 mm); n_{D}^{25} 1.4862.

Preliminary investigations of the chemistry of allenic boranes have revealed that they react with aldehydes to yield the corresponding allenic alcohols, a reaction which is analogous to that previously encountered with allylic boranes.⁸ Thus, dialkyl(1,2-propadienyl)boranes should provide a useful allenic synthon for organic synthesis. We are currently exploring the full scope of the utility of these unsaturated organoboranes in synthesis.

(8) B. M. Mikhailov, *Organometal. Chem. Rev., Sect. A*, **8**, 1 (1972).

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Photochemical Isomerization of 1-Sila-2,4-cyclohexadienes

Sir:

Photoinduced isomerizations of 1,3-cyclohexadienes and the resulting hexatrienes have been studied extensively.¹ Photochemistry of analogous silacyclohexadienes appeared interesting, since the possible products or intermediates should be elusive silahexatrienes² or silacyclopropanes.³ We report here the first examples of photochemical reactions of 1-sila-2,4-cyclohexadienes.

When an evacuated benzene solution of 1,1-dimethyl-2,5-diphenyl-1-sila-2,4-cyclohexadiene (**1**)⁴ was irradiated in an nmr tube,⁵ only a single photoproduct (**2**) was detected. After complete disappearance of **1** (40 hr), the mixture was subjected to a preparative tlc on silica gel to

(1) (a) W. G. Dauben, R. C. Williams, and R. D. McKelvey, *J. Amer. Chem. Soc.*, **95**, 3932 (1973); (b) W. G. Dauben, M. S. Kellogg, J. I. Seeman, N. D. Vietmeyer, and P. H. Wendschuh, *Pure Appl. Chem.*, **33**, 197 (1973); (c) A. Padwa, L. Brodsky, and S. Clough, *J. Amer. Chem. Soc.*, **95**, 6767 (1973); (d) S. W. Spangler and R. P. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972).

(2) The transient existence of $\text{Me}_2\text{Si}=\text{CH}_2$ was indicated by (a) L. E. Gusel'nikov and M. C. Flowers, *Chem. Commun.*, 864 (1968); (b) M. C. Flowers and L. E. Gusel'nikov, *J. Chem. Soc. B*, 419 (1968); (c) T. J. Barton and C. L. McIntosh, *J. Chem. Soc., Chem. Commun.*, 861 (1972). See also ref 8.

(3) Recently, R. L. Lambert, Jr., and D. Seyferth, *J. Amer. Chem. Soc.*, **94**, 9246 (1972), have reported silacyclopropanes. See also D. Seyferth, C. K. Haas, and D. C. Annarelli, *J. Organometal. Chem.*, **56**, C7 (1973).

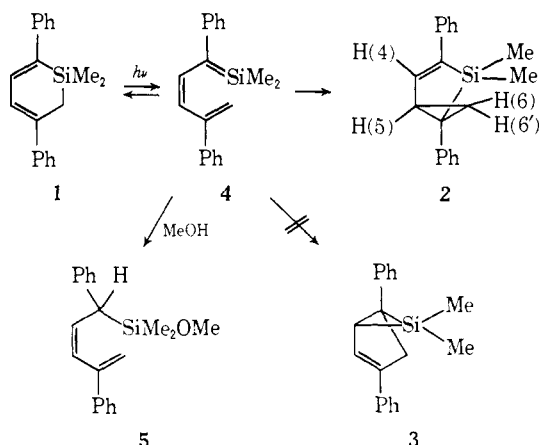
(4) Compound **1** was prepared by reaction of 1,4-dithio-1,4-diphenylbutadiene with dimethyl(chloromethyl)chlorosilane in THF: mp 74–76°; δ (CCl_4) 0.30 (6 H, s, SiMe), 2.00 (2 H, d, H₆, $J_{4,6} = 1.5$ Hz), 6.41 (1 H, dt, H₄, $J_{3,4} = 6.8$ Hz, $J_{4,5} = 1.5$ Hz), 6.86 (1 H, d, H₃, $J_{3,4} = 6.8$ Hz), 7.0–7.5 (10 H, m); $\lambda_{\text{max}}^{\text{n-hexane}}$ 230 (12,000), 340 nm (24,000).

(5) Throughout experiments, a 450-W high-pressure mercury arc lamp was used for irradiation with a Pyrex filter.

afford 2,2-dimethyl-1,3-diphenyl-2-silabicyclo[3.1.0]hex-3-ene (**2**) as an oil in 38% yield.

The structure of this photoproduct, which was followed directly from its spectral properties,^{6,7} represents the product of formal intramolecular (2 + 4) cycloaddition of 2,5-diphenyl-1-sila-1,3,5-hexatriene (**4**). Photochemical ring opening of **1** should result in the formation of **4** in an analogous way to photochemical transformation of 1,3-cyclohexadienes. Silacyclopentane (**3**) is another possible (2 + 4) cycloaddition product from **4** but was not formed. Absence of **3** in the photoproduct may be attributed to instability of a silacyclopentane due to the ring strain.⁸

The intermediacy of **4** was supported by the following trapping experiment with methanol.⁸ The irradiation of **1** in benzene containing a small amount of methanol (2 equiv to **1**) for 2.5 hr under argon atmosphere yielded methoxysilane **5** in 50% yield.⁹ Both **1** and **2** were



inert to methanol without irradiation, and **5** was not formed from **2** even by irradiation under a similar condition. The fact that the rate of disappearance of **1** under irradiation was accelerated by the addition of a trace amount of methanol indicates that a photochemical equilibration was established between **1** and **4**.

Contrary to the diphenyl derivative (**1**), the tetraphenyl derivative (**6**)¹⁰ was found to give a silacyclobutene (**7**) on irradiation. Thus, the nmr spectrum of a benzene solution of **6** irradiated *in vacuo* for 4 hr showed only one photoproduct, **7**, along with unchanged **6**. The 1:1 molar ratio of **7** to **6** remained unchanged for prolonged irradiation (10 hr). Interestingly, by heating the 1:1 mixture of **6** and **7** in benzene at 55° overnight, **7** returned to **6** quantitatively.

The structure of **7** was assigned by its nmr spectrum. At 100 MHz (C_6D_6) **7** had resonances of two singlets at δ 0.33 and 0.59 due to SiMe groups and two doublets at

(6) All compounds were analyzed satisfactorily.

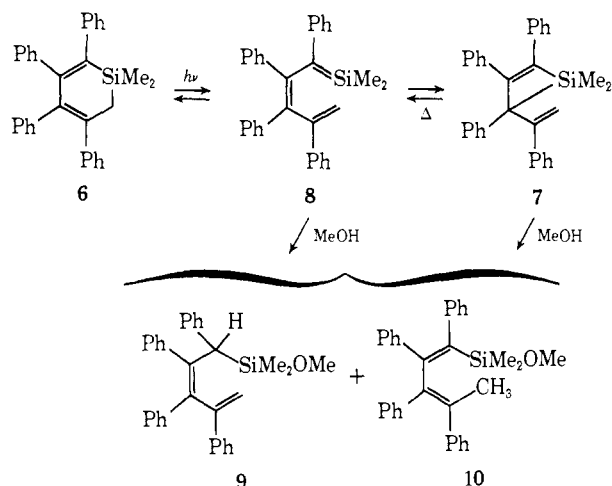
(7) Compound **2**: M^+ 276; $\lambda_{max}^{n-hexane}$ 267 (12,000), 270 nm (12,500); nmr δ (CCl_4) 0.23 (3 H, s, SiMe), 0.44 (3 H, s, SiMe), 0.92 (1 H, t, H_6 , $J_{6,6'} = J_{6,5} = 3.0$ Hz), 1.37 (1 H, d of d, H_5 , $J_{5,6} = 7.5$ Hz, $J_{6,6'} = 3.0$ Hz), 2.31 (1 H, dt H_5 , $J_{5,6} = 7.5$ Hz, $J_{4,5} = J_{5,6'} = 3.0$ Hz), 7.17 (1 H, d, H_4 , $J_{4,5} = 3.0$ Hz), 7.0–7.3 (10 H, m).

(8) (a) P. Boudjouk, J. R. Roberts, C. M. Golino, and L. H. Sommer, *J. Amer. Chem. Soc.*, **94**, 7936 (1972); (b) P. Boudjouk and L. H. Sommer, *J. Chem. Soc., Chem. Commun.*, **54** (1973).

(9) Compound **5**: M^+ 308 (11); m/e 89 (100); nmr δ (CCl_4) -0.03 (6 H, s, Si-Me), 3.21 (3 H, s, OMe), 3.28 (1 H, d, H_2 , $J_{2,3} = 11.5$ Hz), 5.12 (1 H, dd, H_6 , $J_{5,6} = 1.0$ Hz, $J_{6,6'} = 2.0$ Hz), 5.28 (1 H, d, $H_{6'}$, $J_{6,6'} = 2.0$ Hz), 6.03 (1 H, dd, H_3 , $J_{3,2} = 11.5$ Hz, $J_{3,4} = 11.5$ Hz), 6.18 (1 H, d, H_4 , $J_{3,4} = 11.5$ Hz), 6.8–7.3 (10 H, m); $\lambda_{max}^{n-hexane}$ 226 (18,400), 254 sh (9100), 302 (800).

(10) G. Märkl and P. L. Merz, *Tetrahedron Lett.*, 1303 (1971).

δ 5.53 (1 H, $J = 1.0$ Hz) and 5.81 (1 H, $J = 1.0$ Hz) besides multiplets due to phenyl groups. Particularly two doublets are characteristic to those arising from terminal methylene protons. This assignment was further supported by the following chemical transformation. Treatment of the mixture with methanol yielded methoxysilanes **9** and **10** in 14 and 41% yields, respec-



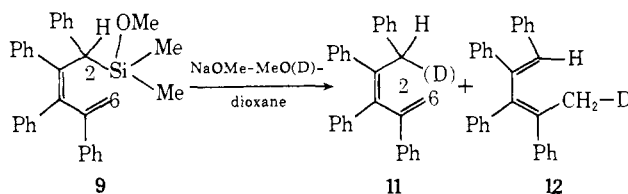
tively, along with **6** which was stable under the condition.¹²

The photochemical formation of silacyclobutene **7** from **6** can be rationalized also by the intervention of a silahexatriene (**8**), and this is substantiated by the trapping experiment. The irradiation of **6** in benzene containing a small amount of methanol (2 equiv of **6**), afforded **9** and **10** in 58 and 17% yield, respectively. The quite different ratio of **9** to **10** from that observed in methanolysis of the silacyclobutene **7** suggests strongly that unstable **8** should be formed first in the photochemical conversion of **6** to **7**.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes. The work was supported in part by a Grant-in-Aid of the Ministry of Education.

(11) Compound **9**: an oil, M^+ 460 (6.5), $M^+ - 89$ (100), $M^+ - 90$ (65.5); nmr δ (CCl_4) -0.04 (3 H, s, Si-Me) 0.07 (3 H, s, Si-Me), 3.29 (3 H, s, OMe), 3.96 (1 H, s, H_2), 5.26 5.80 (2 H, d, $J_{6,6'} = 1.5$ Hz, H_6 , $H_{6'}$), 6.4–7.4 (20 H, m); $\lambda_{max}^{n-hexane}$ 250 (16,200), 279 sh (8900). Compound **10**: an oil, M^+ 460 (5.1), $M^+ - 89$ (17), 89 (100); nmr δ (CCl_4) 0.16, 0.21 (3 H, s, Si-Me), 2.19 (3 H, s, C-Me), 3.31 (3 H, s, OMe), 6.6–7.4 (20 H, m); $\lambda_{max}^{n-hexane}$ 226 sh (20,000), 260 (12,400).

(12) Desilylation of **9** with MeOH or MeOD–MeONa–dioxane at room temperature afforded two dienes **11** and **12** in 75% yield, respectively, whose structures were assigned on the basis of their physical properties. Compound **11**: mp 90–91°; M^+ 372 (14.5); nmr δ (CCl_4) 3.95 (2 H, s, H_2), 5.37, 5.78 (2 H, d, $J_{6,6} = 1.5$ Hz, H_6 , $H_{6'}$), 6.8–7.5 (20 H, m). Compound **12**: mp 138–9°; M^+ 372 (100); nmr δ (CCl_4) 2.07



(3 H, s, C-CH₃), 6.30 (1 H, s, H_2), 6.6–7.4 (20 H, m).

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