Synthesis of Cyclic Silyl Diazo Compounds

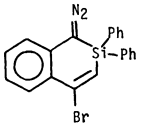
Akira SEKIGUCHI and Wataru ANDO*

Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 305

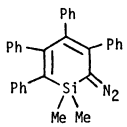
(Received October 23, 1981)

Synopsis. Cyclic silyl diazo compounds, 1-diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene, 6-diazo-1,1-dimethyl-2,3,4,5-tetraphenylsilacyclohexa-2,4-diene, and 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene, were prepared and their spectroscopic properties were determined.

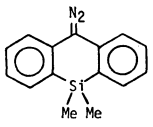
In recent years, interest in the chemistry of silylcarbenes has remarkably increased for the formation of silicon-carbon double bonded intermediates.[1] Simple silyl diazo compounds such as trimethylsilyldiazomethane,[2] ethyl trimethylsilyldiazoacetate,[3] bis(trimethylsilyl)diazomethane,[4] and their derivatives have been synthesized and studied. However, cyclic silyl diazo compounds like 1-diazo-1,2-dihydro-2-silanaphthalene, 6-diazosilacyclohexa-2,4-diene, and 10-diazo-9,10-dihydro-9-silaanthracene, have not been prepared so far. We now wish to report here synthesis of 1-diazo-2,2-diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene (**1**), 6-diazo-1,1-dimethyl-2,3,4,5-tetraphenylsilacyclohexa-2,4-diene (**2**), and 10-diazo-9,9-dimethyl-9,10-dihydro-9-silaanthracene (**3**).



1

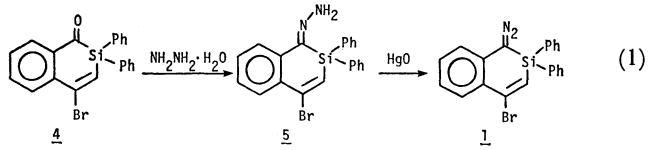


2

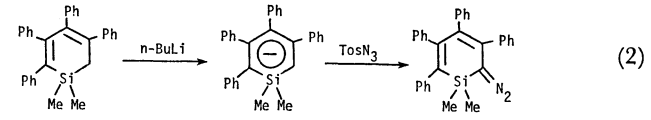


3

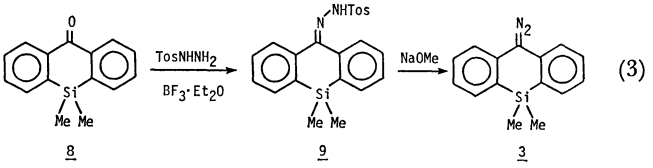
Diazo compound **1** was prepared by the conversion of the silyl ketone **4** to the hydrazone **5** followed by the oxidation with mercury(II) oxide in petroleum ether and benzene in 69% yield (Eq. 1). The spectroscopic data are given in Table . Silyl diazo compound **2** was obtained by a modification of the method of Doering and DePuy.[5] Direct diazo transfer by *p*-toluenesulfonyl azide to the silacyclohexadienyl anion **7** produced the silyl diazo compound **2** as yellow crystals in 36% yield (Eq. 2). Both **1** and **2** are relatively stable enough to be recrystallyzed. Diazo compound **3** was prepared as described in Eq. 3. Tosylhydrazone **9** was synthesized by the reaction of the ketone **8** with tosylhydrazine in ethanol in the presence of $BF_3 \cdot Et_2O$. The reaction is too slow in the absence of the catalyst. Treatment of the hydrazone **9** with sodium methoxide in pyridine afforded the diazo compound **3** in 90% yield as purple crystals.



(1)



(2)



(3)

TABLE 1. SPECTROSCOPIC DATA OF CYCLIC SILYL DIAZO COMPOUND

Diazo compd	NMR (CCl_4, δ)	IR (KBr, $\nu(N_2)$/cm^{-1})	UV λ_{max}/nm (C_6H_6, ε)
1	6.70—8.17 (m, ArH and BrC=CHSi)	2030	318 (4.69×10^3) 333 (4.78×10^3) 360 (6.96×10^3)
2	0.43(s, 6H, $SiMe_2$), 6.37—7.33(m, 20H, ArH)	2025	377 (1.17×10^4)
3	0.43(s, 6H, $SiMe_2$), 6.90—7.70(m, 8H, ArH)	2030	297 (1.73×10^4) 309 (1.87×10^4) 537 (52.0)

Experimental

General. NMR spectra were recorded on a Varian EM 360A spectrometer. IR and UV spectra were obtained by a Hitachi 260-50 spectrometer and a Shimadzu UV-365 spectrometer, respectively.

Materials. 2,2-Diphenyl-4-bromo-1,2-dihydro-2-silanaphthalene-1-one (**4**),[6] 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclohexa-2,4-diene (**6**),[7] and 9,9-dimethyl-9,10-dihydro-9-silaanthracene-10-one (**8**),[8] were prepared by known procedures as referenced.

Synthesis of Hydrazone ***9***. Tosylhydrazone **9** was prepared in 32% yield by dissolving the ketone **8** (4.76 g, 20.0 mmol) in ethanol, adding excess tosylhydrazine (8.44 g, 45.4 mmol) and *ca.* 1 mL of $BF_3 \cdot Et_2O$ and refluxing for 3 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel with benzene/chloroform. Evaporation of the solvent afforded crude product **9** which was recrystallyzed from ethanol to give white crystals (2.63 g, 6.48 mmol), mp 168—169.5 °C. Found: C, 65.01; H, 5.44; N, 6.94%. Calcd for $C_{22}H_{22}N_2O_2SSi$: C, 64.99; H, 5.45; N, 6.89%.

Synthesis of ***1***. Hydrazine hydrate (16 g, 320 mmol) was added to a mixture of ethanol and benzene containing the silyl ketone **4** (10 g, 25.6 mmol) and a few drops of acetic acid at 0 °C. After stirring for 1.5 h, the reaction mixture was poured into water, and extracted with benzene. Hydrazone **5** was used without isolation. The benzene solution of **5** was diluted with petroleum ether, and then mercury(II) oxide (20 g, 92.3 mmol) was added. After stirring for 24 h, precipitated mercury was filtered off and the filtrate was concentrated. The residue was chromatographed on silica gel containing 10% water at 0 °C with petroleum ether/carbon tetrachloride. Evaporation of the solvent gave crude product **1** which was recrystallyzed from benzene/ethanol to give yellow-orange crystals (7.1 g, 69%), mp 129—130

°C. Found: C, 62.47; H, 3.69; N, 7.05; Br, 20.10%. Calcd for $C_{21}H_{15}N_2SiBr$: C, 62.53; H, 3.74; N, 6.94; Br, 19.81%.

Synthesis of ***2***. 1,1-Dimethyl-2,3,4,5-tetraphenylsilacyclohexa-2,4-diene (**6**) (7.0 g, 16.4 mmol) was treated with equimolar amount of butyllithium in THF at 0 °C. The red silacyclohexadienyl anion **7** was formed immediately. The anion was slowly added to a solution of *p*-toluenesulfonyl azide (3.9 g, 19.8 mmol) in THF at −78 °C, and the reaction mixture was slowly warmed to room temperature. The mixture was poured into water, and extracted with hexane. Chromatography on silica gel containing 10% water at 0 °C with hexane/benzene gave crude product **2** which was recrystallyzed from ethanol/benzene to give yellow crystals (2.7 g, 36%), mp(decomp) 134.5—135.5 °C. Found: C, 81.90; H, 5.65%. Calcd for $C_{31}H_{26}N_2Si$: C, 81.89; H, 5.76%.

Synthesis of ***3***. Tosylhydrazone **9** (1.00 g, 2.46 mmol) was dissolved in pyridine, and sodium methoxide (0.278 g, 5.15 mmol) was added to the solution. The mixture was heated at 70 °C for 15 min. The resulting red solution was poured into water, and extracted with hexane. Chromatography on silica gel containing 10% water at 0 °C with hexane gave purple crystals (0.554 g, 90%), mp 96—97 °C. Found: C, 72.07; H, 5.64; N, 11.05%. Calcd for $C_{15}H_{14}N_2Si$: C, 71.95; H, 5.63; N, 11.18%.

References

1) A. Sekiguchi and W. Ando, *J. Am. Chem. Soc.*, **103**, 3579 (1981), and references cited therein.

2) D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Am. Chem. Soc.*, **90**, 1080 (1968).

3) U. Schöllkopf and N. Rieber, *Angew. Chem.*, **79**, 906 (1967).

4) D. Seyferth and T. C. Flood, *J. Organomet. Chem.*, **29**, C25 (1971).

5) W. E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

6) R. Corriu and J. P. Masse, *J. Organomet. Chem.*, **22**, 321 (1970).

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

8) J. Y. Corey, M. J. Dye, R. L. Farrell, and M. V. Mitchell, *J. Organomet. Chem.*, **153**, 127 (1978).