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1,1-Dimesityl-1-silacyclopenta-2,4-diene: A stable carbon-unsubstituted silole

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Abstract

1,1-Dimesityl-1-silacyclopenta-2,4-diene, a stable carbon-unsubstituted silole, has been prepared by the dehydration of 1,1-dimesityl-1-silacyclopent-4-en-3-ol. Also described are the reactions of the titled compound with maleic anhydride, triazolinedione and diiron nonacarbonyl.

1. Introduction

Silacyclopentadienes (siloles) have been playing important roles in the development of modern organosilicon chemistry (for reviews see refs. 1). Carbon-unsubstituted Group 14 metalloles have been one of the most interesting synthetic targets in these decades, challenged by several research groups [2]. The hitherto known carbon-unsubstituted siloles **1a** and **1b**, however, undergo spontaneous [2 + 4] dimerization at room temperature [2]. Meanwhile, stable carbon-unsubstituted germole [3] and stannole [4] were prepared via a palladium-catalysed reaction and a coupling reaction of 1,4-dilithiobutadiene respectively. In connection with our continuing research on the synthesis and properties of metallacyclic compounds [5], we now report the preparation of the titled compounds as the first example of a carbon-unsubstituted silole kinetically stabilized by introduction of bulky substituents into the silicon atom.

Successful synthesis of 1,1-dimesitylsilole (**2**) was conducted according to the procedure of Dubac et al. [2f] as outlined in Scheme 1. 1,1-Dimesityl-1-silacyclopent-3-ene (**3**) [6] was readily converted to 1,1-dimesityl-1-silacyclopent-4-en-3-ol (**4**) by singlet oxygen oxidation followed by treatment with $NaBH_4$ with 30% yield. Dehydration of **4** through the corresponding S-methylxanthate (**5**) afforded the desired silole **2** with a 35% yield, as colourless crystals. Treatment of **4** with thionyl chloride also gave **2**, but with lower yield (23%). The structural assignment of **2** is based on its spectroscopic data. In the ^1H nuclear magnetic resonance (NMR) spectrum, **2** showed the characteristic AA′XX′ pattern centred at 6.35 and 6.95 ppm. Even when heated for 5 h at 100°C in toluene, the silole **2** did not dimerize at all and was recovered quantitatively. Certainly, the two mesityl groups are effective for inhibition of [2 + 4] cyclodimerization.

The structure of **2** was further confirmed by chemical transformation as follows. Reactions of **2** with maleic anhydride and 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) took place rapidly at room temperature to afford the corresponding Diels–Alder cycloadducts **6** (96%) and **7** (86%) respectively. Upon heating with diiron nonacarbonyl in refluxing benzene, **2** was converted to the expected diene complex **8**, with a 67% yield, as yellow crystals.

2. Experimental details

NMR spectra were recorded with a JEOL JNM-GX270 spectrometer. Deuterated chloroform was used as the solvent. Mass spectral data were obtained on a Shimadzu QP-1000 and a JEOL LMS-D300 mass spectrometer. IR spectra were recorded with a JASCO FT/IR-5000 spectrometer. Preparative column chromatography was performed using Kieselgel 60 (Merck)

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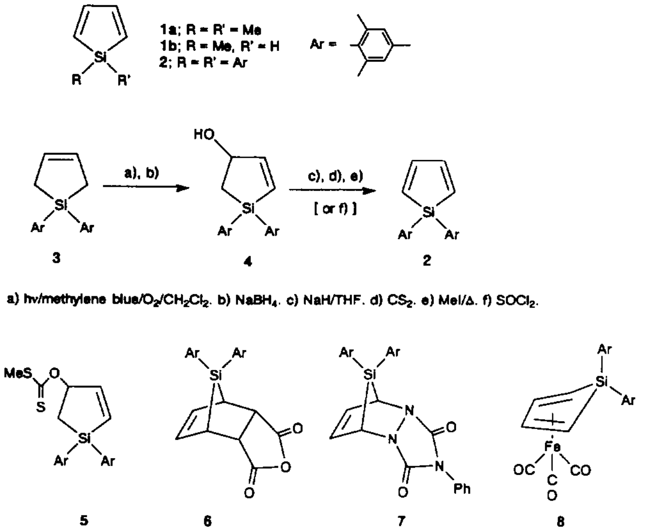

Scheme 1.

and Wakogel C-300 (Wako Pure Chemical). Reagent-grade solvents were used for the experiments. Hexane, benzene, toluene and methylene chloride were dried over calcium hydride and distilled before use. Tetrahydrofuran (THF) was refluxed on benzophenone ketyl and distilled before use. Methylene blue (Wako Pure Chemical), maleic anhydride (Wako Pure Chemical), 4-phenyl-1,2,4-triazoline-3,5-dione (Aldrich) and diiron nonacarbonyl (Kanto Chemicals) were used as received.

2.1. *Preparation of 1,1-dimesitylsilacyclopent-3-ene [6,7]*

In freshly distilled THF (200 ml), $MgCl_2$ (9.52 g, 100 mmol), finely cut Li (1.24 g, 0.18 g-atom) and naphthalene (6.1 g, 47.7 mmol) were stirred overnight at room temperature. The resulting magnesium slurry was allowed to settle for 3 h, and the supernatant was drawn off via a syringe. Freshly distilled THF (200 ml) was added, followed by an excess amount of 1,3-butadiene (about 10 ml) and dimesityldichlorosilane (7.66 g, 22.7 mmol). After stirring for 48 h, the solution was hydrolysed and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and then concentrated *in vacuo*. Subsequent silica gel flash chromatography using hexane as eluent afforded 3.5 g (49%) of **3** [6], ^{1}H NMR ($CDCl_3$); 6.79 (s, 4H, CH^{Ar}), 6.03 (t, 2H, $J=$ 1.3 Hz, $SiCH_2CH$), 2.34 (s, 12H, o-Me^{Ar}), 2.24 (s, 6H, p-Me^{Ar}), 2.04 (d, 4H, $J=1.3$ Hz, $SiCH_2$) ppm. Mass spectroscopy (MS) (relative intensity): 320(1), 251(10), 200(100), 146(99).

2.2. *Photo-oxygenation of 3*

A solution of **3** (1.4 g, 4.4 mmol) and methylene blue (20 mg) in CH_2Cl_2 (40 ml) was irradiated with two 500 W halogen–tungsten lamps in a water-cooling bath while an oxygen flow passed through the solution. After consumption of **3**, the solution was treated with 1.3 g of $NaBH_4$ and then stirred overnight. Subsequent flash column chromatography using CH_2Cl_2 afforded **4** with a 30% yield (colourless oil). ^{1}H NMR ($CDCl_3$): 6.78 (dd, 1H, $J_{A'B'}=9.7$ Hz, $J_{B'X'}=1.5$ Hz, SiCHCH), 6.76 (s, 4H, CH^{Ar}), 6.52 (dd, 1H, $J_{A'B'}=9.7$ Hz, $J_{B'X'}=1.5$ Hz, SiCHCH), 4.93 (m, 1H, HCOH), 2.34 (s, 6H, o-Me^{Ar}), 2.33 (s, 6H, o-Me^{Ar}), 2.30 (dd, 1H, $J_{AB}=$ 7.0 Hz, $J_{BX}=14.9$ Hz, $SiCH_2$), 2.23 (s, 3H), 2.21 (s, 3H), 1.59 (brs, 1H), 1.20 (dd, 1H, $J_{AX}=14.9$ Hz, $J_{AB}=$ 7.0 Hz, $SiCH_2$) ppm. ^{13}C NMR ($CDCl_3$): 152.82 (d, SiCHCH), 143.44 (s, C^{Ar}), 143.29 (s, C^{Ar}), 138.96 (s, C^{Ar}), 138.85 (s, C^{Ar}), 135.06 (d, SiCHCH), 132.99 (s, C^{Ar}), 132.01 (s, C^{Ar}), 129.11 (d, HC^{Ar}), 128.95 (d, HC^{Ar}), 75.68 (d, HCOH), 27.50 (t, $SiCH_2$), 23.82 (q, o-Me^{Ar}), 23.70 (q, o-Me^{Ar}), 20.98 (q, p-Me^{Ar}), 20.92 (q, p-Me^{Ar}) ppm. IR (neat): 3400 cm^{-1}. MS m/z (relative intensity): 336(57), 319(54), 291(32), 216(67), 199(100): Anal. Exact mass found: 336.1895. $C_{22}H_{28}OSi$ calc.: 336.1909.

2.3. *Dehydration of 4 [2f]*

A solution of alcohol **4** (818 mg, 2.43 mmol) in THF (5 ml) was added dropwise with stirring over 5 min to a suspension of NaH (200 mg, 4.86 mmol) in THF (10 ml) at 0°C. The mixture was stirred for 30 min. To the resulting solution was added dropwise CS_2 (2889 mg, 3.80 mmol) and then MeI (566 mg, 4.00 mmol). After heatings to reflux for 4 min, the solution was concentrated *in vacuo*. Pure **2** was obtained with a 36% yield by silica gel flash column chromatography using hexane as eluent. Low temperature recrystallization from hexane–ethanol gave colourless plates of **2** (melting point (m.p.) 89–92°C). ^{1}H-NMR ($CDCl_3$): 6.95 (AA'XX', 2H, $J_{AX}=J_{A'X'}=9.2$ Hz, $J_{AX'}=J_{A'X}=2.2$ Hz, SiCHCH), 6.78 (s, 4H, HC^{Ar}), 6.50 (AA'XX', 2H, SiCHCH), 2.34 (s, 12H, o-Me^{Ar}), 2.22 (s, 6H, p-Me^{Ar}) ppm. ^{13}C NMR ($CDCl_3$): 144.45 (s, C^{Ar}), 144.01 (d, SiCHCH), 138.79 (s, C^{Ar}), 132.96 (d, SiCHCH), 129.28 (s, C^{Ar}), 128.82 (d, HC^{Ar}), 24.43 (q, o-Me^{Ar}), 20.99 (q, p-Me^{Ar}). IR (KBr): 1600, 1440 cm^{-1}. MS m/z (relative intensity): 318(100), 198(58), 147(49), Anal. Found: C, 82.68; H, 8.19. $C_{22}H_{26}Si$ calc.: C, 82.96; H, 8.23%.

2.4. *Dehydration of 3 using $SOCl_2$*

To a stirred pyridine (10 ml) solution of **4** (420 mg, 1.25 mmol), was added dropwise 142 mg (1.2 mmol) of $SOCl_2$ at 0°C. After hydrolysis, the organic layer was extracted with ether and dried over anhydrous $MgSO_4$. Pure **2** was obtained with a 23% yield by the same procedure described above.

2.5. Reaction of 2 with maleic anhydride

A $CDCl_3$ (0.4 ml) solution of **2** (40.7 mg, 0.129 mmol) and maleic anhydride (16.4 mg, 0.167 mmol) was kept standing for 1 h. NMR analysis indicated that the reaction was complete and **6** was formed quantitatively. Pure samples of **6** were obtained by recrystallization from hexane with a 96% yield (m.p., 215–217°C). ^1H NMR ($CDCl_3$): 6.83 (s, 2H, CH^{Ar}), 6.81 (s, 2H, CH^{Ar}), 6.43 (dd, 2H, SiCHC*H*=), 3.62 (s, 2H, SiCH), 3.13 (brs, 2H, CHCO), 2.50 (s, 6H, *o*-Me^{Ar}), 2.46 (s, 6H, *o*-Me^{Ar}), 2.23 (s, 3H, *p*-Me^{Ar}), 2.22 (s, 3H, *p*-Me^{Ar}) ppm. ^{13}C NMR ($CDCl_3$): 173.63 (s, CO), 144.60 (s, C^{Ar}), 143.48 (s, C^{Ar}), 140.29 (s, C^{Ar}), 140.15 (s, C^{Ar}), 136.48 (s, C^{Ar}), 132.60 (d, SiCHC*H*=), 129.56 (d, HC^{Ar}), 129.28 (d, HC^{Ar}), 46.45 (d, *C*HCO), 37.58 (d, SiCH), 23.97 (q, *o*-Me^{Ar}), 22.87 (q, *o*-Me^{Ar}), 20.96 (q, *p*-Me^{Ar}), 20.94 (q, *p*-Me^{Ar}) ppm. IR (KBr): 1850, 1770 cm^{-1}. MS *m/z* (relative intensity): 387(72), 267(39), 163(82), 147(100). Anal. Found: C, 74.71; H, 6.78. $C_{26}H_{28}O_3Si$ calc.: C, 74.96; H, 6.77%.

2.6. Reaction of 2 with 4-phenyl-1,2,4-triazoline-3,5-dione

To a $CDCl_3$ (0.4 ml) solution of **2** (50 mg, 0.16 mmol) in an NMR tube was added 12.1 mg (0.069 mmol) of PTAD at room temperature. The characteristic red colour of PTAD disappeared immediately. Recrystallization of the reaction mixture from hexane afforded 26.6 mg (86%) of **7** as colourless solids. ^1H NMR ($CDCl_3$): 7.43–7.35 (m, 5H, Ph), 6.86 (s, 2H, CH^{Ar}), 6.83 (s, 2H, CH^{Ar}), 6.64 (dd, 2H, SiCHC*H*=), 5.04 (dd, 2H, SiC*H*), 2.59 (s, 6H, *o*-Me^{Ar}), 2.44 (s, 6H, *o*-Me^{Ar}), 2.25 (s, 3H, *p*-Me^{Ar}), 2.24 (s, 3H, *p*-Me^{Ar}) ppm. ^{13}C NMR ($CDCl_3$): 158.12 (s, CO), 144.44 (s)*, 144.27 (s)*, 140.91 (s)*, 140.64 (s)*, 132.08 (d)*, 131.85 (s)*, 129.40 (d)*, 129.24 (d)*, 129.01 (d)*, 128.08 (d)*, 127.51 (s)*, 125.54 (d)*, 124.97 (s)*, 55.50 (d, Si*C*H), 23.76 (q, *o*-Me^{Ar}), 22.97 (q, *o*-Me^{Ar}), 21.09 (q, *p*-Me^{Ar}), 21.02 (q, *p*-Me^{Ar}) ppm. The signals with asterisks are assigned to mesityl, phenyl and olefinic sp_2 carbons. MS *m/z* (relative intensity); 493(10), 478(60), 374(21), 147(100), 119(76). Anal. Exact mass found: 493.2212. $C_{30}H_{31}N_3O_2Si$ calc.: 493.2186.

2.7. Reaction of 2 with diiron nonacarbonyl

A benzene solution of **2** (50 mg, 0.16 mmol) and diiron nonacarbonyl (120 mg, 0.33 mmol) was refluxed for 10 min under a N_2 atmosphere. The solution turned green immediately. Yellow crystals of **8** were obtained by recrystallization from hexane with a 67% yield (m.p., 185–187°C). ^1H NMR ($CDCl_3$): 6.84 (s, 2H, HC^{Ar}), 6.66 (s, 2H, HC^{Ar}), 5.77 (AA′XX′, 2H, SiCHC*H*), 2.53 (s, 6H, *o*-Me^{Ar}), 2.42 (s, 6H, *o*-Me^{Ar}), 2.32 (AA′XX′, 2H, SiC*H*CH), 2.27 (s, 3H, *p*-Me^{Ar}), 2.17 (s, 3H, *p*-Me^{Ar}) ppm. ^{13}C NMR ($CDCl_3$): 211.37 (s, CO), 144.17 (s, C^{Ar}), 142.08 (s, C^{Ar}), 139.24 (s, C^{Ar}), 138.70 (s, C^{Ar}), 137.05 (s, C^{Ar}), 131.34 (s, C^{Ar}), 129.09 (d, HC^{Ar}), 128.98 (d, HC^{Ar}), 90.33 (d, SiCH*C*H), 50.69 (d, Si*C*HCH), 24.06 (q, *o*-Me^{Ar}), 23.70 (q, *o*-Me^{Ar}), 21.11 (q, *p*-Me^{Ar}), 20.88 (q, *p*-Me^{Ar}) ppm. IR (KBr): 2050, 1970 cm^{-1}. MS *m/z* (relative intensity): 431(2), 403(11), 375(50), 254(100). Anal. Found: C, 65.72; H, 5.89. $C_{25}H_{26}O_3SiFe$ calc.: C, 65.50; H, 5.72%.

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