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LETTERS

Benzosilacyclohexadienones: synthesis and reactivity

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Abstract

The synthesis and the allylic oxidation reaction of new benzosilacyclohexenes are described. The reactivity of these new cyclic β -silyl- α,β -unsaturated ketones in cycloaddition reactions, as well as in 1,4-addition reactions, is discussed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: benzosilacyclohexenes; allylic oxidation; cyclic β -silyl- α,β -unsaturated ketones; Diels–Alder reaction; cyanocuprate addition; 1,4-addition; Mukaiyama reaction; zinc bromide catalyst.

Although the literature describes several examples of β -silyl- α,β -unsaturated ketones,¹ there are no reports of the synthesis and reactions of benzosilacyclohexadienones as represented by the 1,1-diphenyl and 1,1-dimethyl compounds **1** and **2**, respectively. (Fig. 1). We describe the first synthesis of these dienones and report their reactivity toward nucleophiles and in Diels–Alder reactions.

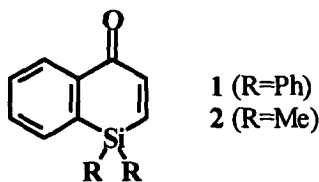


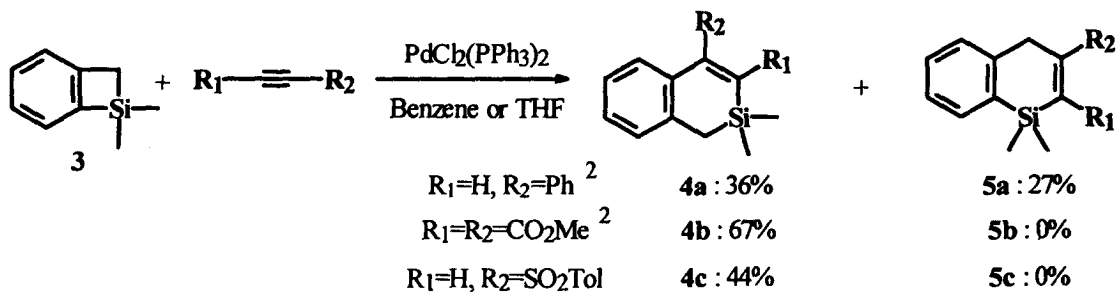
Figure 1.

1. Synthesis of 1-silyl-1,4-dihydronaphthalene precursors

Our route to silyldienones **1** and **2** envisioned allylic oxidation of 1-silyl-1,4-dihydronaphthalene precursors. We initially investigated the known Pd-catalyzed insertion of certain conjugated alkynes into a C–Si σ -bond of benzosilacyclobutene **3**² (Scheme 1). To this end, tosylacetylene (an acetylene

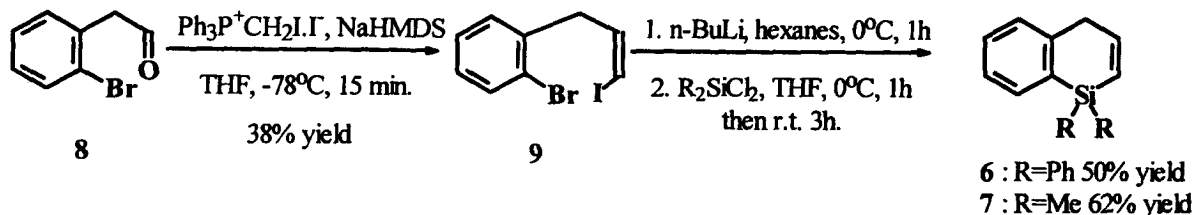
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equiv.)³ was reacted with **3** at 50°C and found to give 44% of the single undesired regioisomer **4c**, m.p. 166–168°C, as confirmed by single crystal X-ray analysis.^{4,5}



Scheme 1.

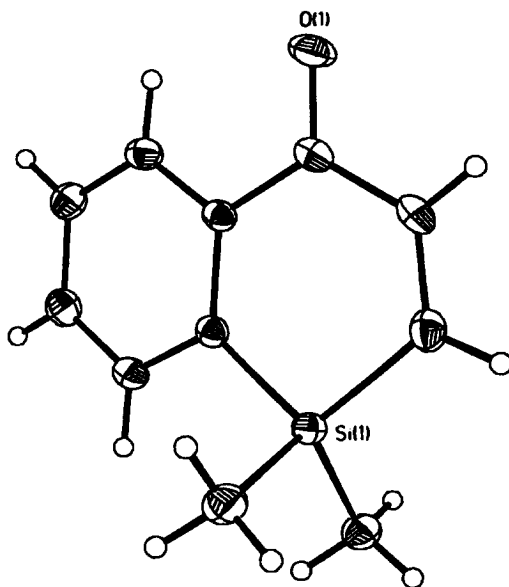
Therefore the 1-silyl-1,4-dihydronaphthalenes **6** and **7** were prepared from 2-bromophenylacetaldehyde **8**⁶ by Wittig reaction with $\text{ICH}_2\text{P}^+\text{PH}_3\text{I}^-$ under lithium-free conditions to give cleanly the *Z*-iodoalkene **9**.⁷ Double halogen–metal exchange with excess *n*-BuLi in hexanes,⁸ followed by ring closure with Ph_2SiCl_2 or Me_2SiCl_2 , led to the 1-silyl-1,4-dihydronaphthalenes **6** and **7**⁹ in yields of 50% and 62%, respectively (Scheme 2). The multigram synthesis of regiochemically pure **6** and **7** was required for anticipated use in the synthesis of group (IV) metallocene analogues.¹⁰



Scheme 2.

2. Preparation of benzosilacyclohexadienones

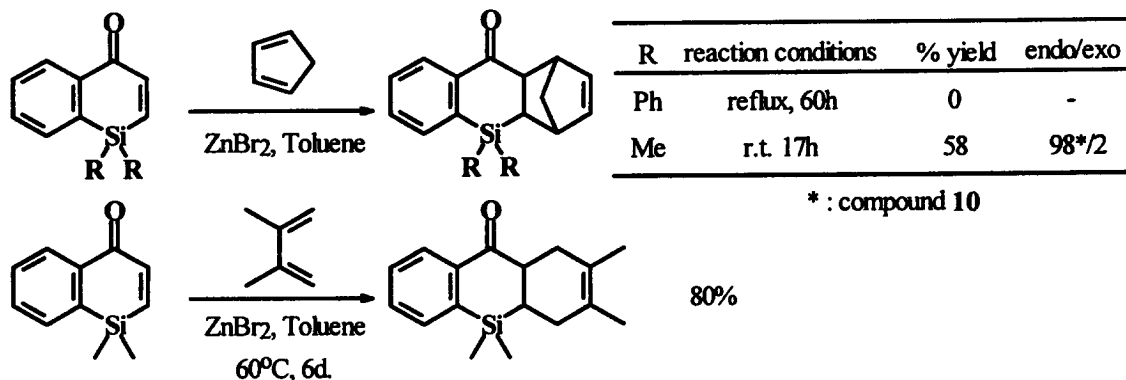
Allylic oxidation of **6** using SeO_2 in refluxing ethanol for 24 h^{1a} proceeded to give a 40% yield of the benzosilacyclohexadienone **1**.¹¹ These conditions proved to be too harsh for substrate **7**. However, the reaction of **7** with 0.5 equiv. SeO_2 in the presence of *t*-BuOOH at rt in CH_2Cl_2 ¹² for 40 h did yield the sensitive dimethylsilyl compound **2**, m.p. 50–51°C, in a 40% yield.¹³ The structure of **2** was confirmed by single crystal X-ray structure determination as shown.^{4,14}



2

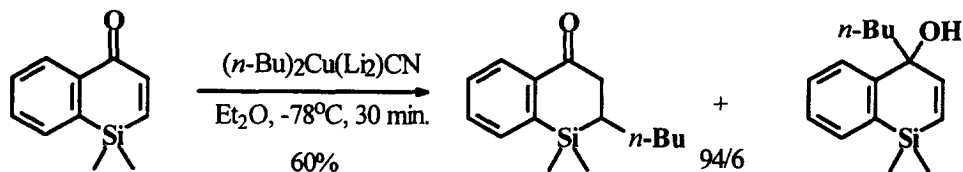
3. Reactivity of benzosilacyclohexadienones

Literature precedent¹⁵ suggests that acyclic β -silyl- α,β -unsaturated ketones can act as dienophiles under ZnBr_2 catalysis at 0°C . In contrast, the diphenylsilyl dienone **1** failed to react with cyclopentadiene in refluxing toluene over 60 h even in the presence of ZnBr_2 . On the other hand, the dimethylsilyl dienone **2** reacts with cyclopentadiene in the presence of ZnBr_2 at room temperature, with a high *endo*-selectivity (98/2). The *endo* configuration of the major isomer **10**, m.p. $48\text{--}49^\circ\text{C}$, has been established by a single crystal structure determination.^{4,16} Furthermore, the cycloaddition reaction of **2** with 1,3-dimethyl-1,3-butadiene takes place in 6 days at 60°C leading to the expected cycloadduct in an 80% yield (Scheme 3). This reactivity can be explained by the low energy level of the LUMO orbital of the silyl enone moiety.¹⁷



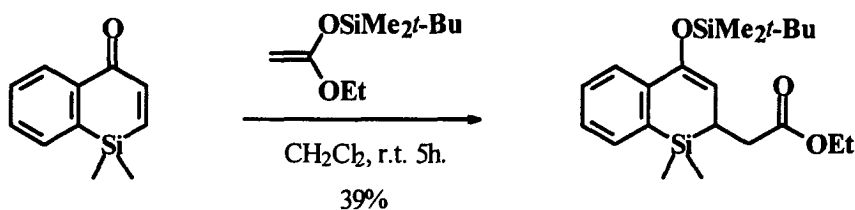
Scheme 3.

The dimethyldienone **2** undergoes conjugate addition with cyanocuprate $(n\text{-Bu})_2\text{Cu}(\text{Li})_2\text{CN}^{18}$ in ether at -78°C (Scheme 4). After 30 minutes, the products of 1,4- and 1,2-addition were obtained in a ratio of 94/6 and in a 60% combined yield.



Scheme 4.

To the best of our knowledge, no Michael–Mukaiyama addition has ever been reported to β -silyl- α,β -unsaturated ketones, a reaction which we observed when dimethyldienone **2** was treated with *O*-ethoxy-*O'*-*t*-butyldimethylsilyloxy ketene acetal¹⁹ in the presence of zinc bromide. After 5 h at room temperature, a 39% yield of the expected silyl enol ether was isolated when 3 equiv. of the silyl ketene acetal were used (Scheme 5).



Scheme 5.

Acknowledgements

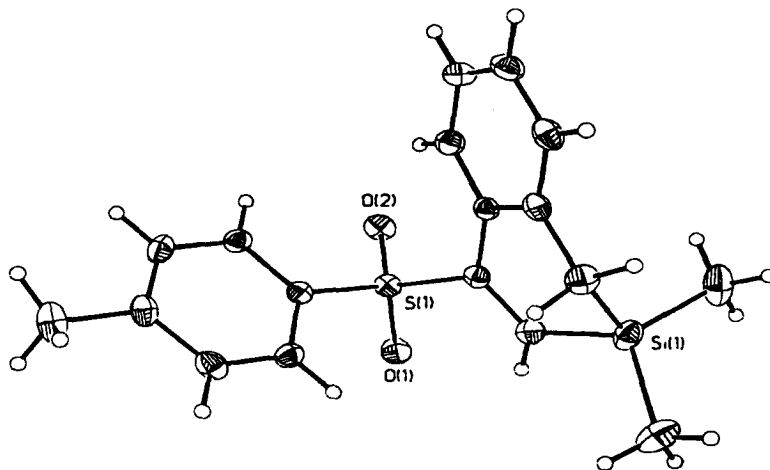
We thank the Dow Chemical Co. for a research grant to C.M.M. and Drs. W. J. Kruper and P. Nickias for helpful discussions.

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- The X-ray intensity data for compounds **4c**, **2** and **10** were collected on a Standard Siemens SMART CCD Area Detector System equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). The structures were solved by direct methods and refined employing full-matrix least-squares on F^2 (Siemens, SHELXTL, version 5.04). The non-*H* atoms for all the structures were refined with anisotropic thermal parameters. The *H* atoms were located and

their positions and isotropic thermal parameters were refined for compounds **2** and **10**, and for compound **4c** the *H* atoms were included in idealized positions.

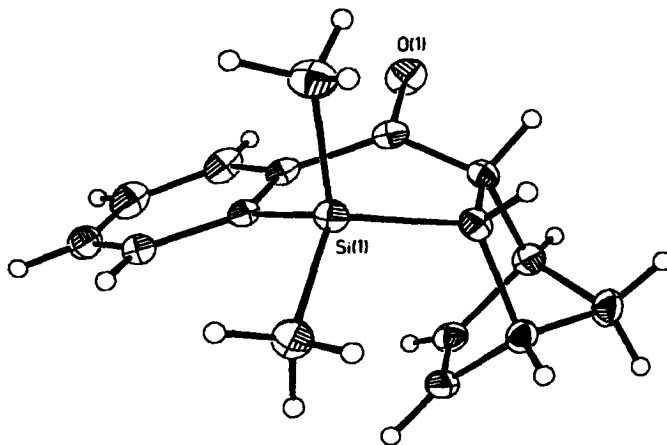
5. Compound **4c**: Monoclinic crystal system; $P2_1/c$ space group; $a=16.4740(10)$ Å, $b=8.8170(6)$ Å, $c=11.9286(8)$ Å, $\beta=95.5780(10)^\circ$; $V=1724.4(2)$ Å³; $D(\text{calc.})=1.265$ g/mm³; $Z=4$; $F(000)=696$; $\lambda=0.71073$ Å; $T=193(2)$ K; crystal size= $0.22\times 0.34\times 0.38$ mm³; $2.48<\theta<23.27^\circ$; reflections collected: 7022, independent: 2446, observed: 2107; final *R* values ($I>2\sigma(I)$): $R_1=0.0395$, $wR_2=0.0885$; *R* indices (all data): $R_1=0.0510$, $wR_2=0.0942$; GOF: 1.048; extinction coeff.= $0.0105(10)$; largest peak: 0.240 e⁻/Å³; hole: -0.281 e⁻/Å³.



4c

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9. Compound **7**: ¹H NMR (CDCl₃, ppm): 7.51–7.10 (4H, mult.); 6.89 (1H, d, *J*=14.5 Hz, *J*=3.9 Hz); 6.03 (1H, dt, *J*=14.5 Hz, *J*=2.1 Hz); 3.65 (2H, dd, *J*=3.9 Hz, *J*=2.1 Hz); 0.27 (6H, s). ¹³C NMR (CDCl₃, ppm): 145.7; 144.2; 134.5; 133.3; 128.6; 128.3; 126.0; 125.4; 36.37; 0.96. MS (EI): 174 (M⁺), 159, 143, 131. HR-MS (EI): found: 174.0859.
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11. Compound **1**: ¹H NMR (CDCl₃, ppm): 8.28 (1H, d); 7.58–7.27 (14H, mult.); 7.15 (1H, d, *J*=8.7 Hz). ¹³C NMR (CDCl₃, ppm): 188.0; 148.0; 143.7; 141.8; 135.5; 135.3; 135.0; 131.8; 131.7; 130.5; 130.4; 129.0; 128.3. MS (EI): 312 (M⁺), 235. HR-MS (EI): found: 312.0974.
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13. Compound **2**: M.p.: 50–52°C; ¹H NMR (CDCl₃, ppm): 8.22 (1H, mult.); 7.55–7.4 (3H, mult.); 7.12 (1H, d, *J*=14.8 Hz); 7.0 (1H, d, *J*=14.7 Hz); 0.3 (6H, s). ¹³C NMR (CDCl₃, ppm): 188.0; 146.9; 146.8; 139.7; 139.3; 133.1; 131.6; 129.8; 128.7; –2.4. IR (neat, cm⁻¹): 3274, 3050, 2959, 2898, 1948, 1845, 1677, 1643, 1578, 1433. HR-MS (EI): found: 188.0653.
14. Compound **2**: Monoclinic crystal system; $P2_1/n$ space system; $a=7.9904(2)$ Å, $b=11.6077(3)$ Å, $c=11.1694(2)$ Å, $\beta=102.2980(10)^\circ$; $V=1012.19(4)$ Å³; $D(\text{calc.})=1.236$ g/mm³; $Z=4$; $F(000)=400$; $\lambda=0.71073$ Å; $T=193(2)$ K; crystal size= $0.10\times 0.18\times 0.40$ mm³; $2.56<\theta<28.39^\circ$; reflections collected: 6007, independent: 2360, observed: 1963; absorption correction: SADABS; final *R* values ($I>2\sigma(I)$): $R_1=0.0389$, $wR_2=0.0987$; *R* indices (all data): $R_1=0.0508$, $wR_2=0.1039$; GOF: 1.055; largest peak: 0.330 e⁻/Å³; hole: -0.301 e⁻/Å³.
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16. Compound **10**: Orthorhombic crystal system; *Pbca* space group; $a=8.13130(10)$ Å, $b=14.18830(10)$ Å, $c=23.8537(2)$ Å, $\beta=90.0(10)^\circ$; $V=2751.99(5)$ Å³; $D(\text{calc.})=1.228$ g/mm³; $Z=8$; $F(000)=1088$; $\lambda=0.71073$ Å; $T=193(2)$ K; crystal size= $0.24\times 0.36\times 0.38$ mm³; $1.71 < \theta < 28.22^\circ$; reflections collected: 15107, independent: 3280, observed: 2620; absorption coeff.= 0.156 mm⁻¹; absorption correction: SADABS (empirical); final *R* values ($I > 2\sigma(I)$): $R_1=0.0405$, $wR_2=0.1017$; *R* indices (all data): $R_1=0.0579$, $wR_2=0.1084$; extinction coeff.: $0.0118(12)$; GOF: 1.079; largest peak: 0.357 e⁻/Å³; hole: -0.394 e⁻/Å³.



10

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