Pergamon

Tetrahedron Letters 40 (1999) 7901–7906

TETRAHEDRON
LETTERS

Benzosilacyclohexadienones: synthesis and reactivity

Andrew S. Kende,* Catherine M. Mineur and Rene J. Lachicotte

Department of Chemistry, University of Rochester, Rochester, NY 14627, USA

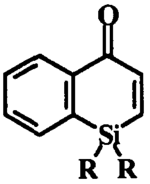
Received 29 June 1999; accepted 19 July 1999

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.



1 (R=Ph)
2 (R=Me)

Figure 1.

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

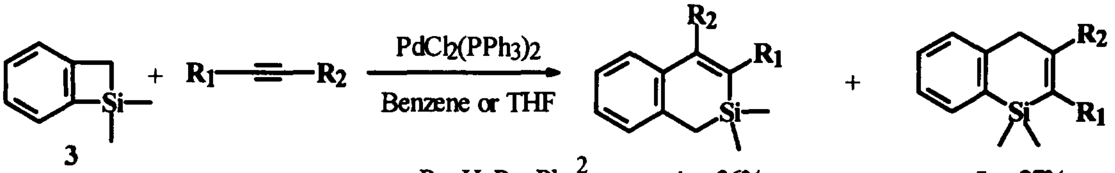
Our route to silyldienones **1** and **2** envisioned allylic oxidation of 1-silyl-1,4-dihydronaphthalene precursors. We initially investigated the known Pd-catalyzed insertion of certain conjugated alkynes into a C–Si σ-bond of benzosilacyclobutene **3**[2] (Scheme 1). To this end, tosylacetylene (an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

---

* Corresponding author.

PII: S0040-4039(99)01494-X

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]

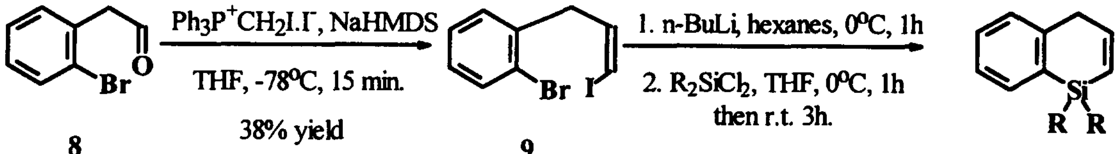


3

R_1=H, R_2=Ph [2]	**4a** : 36%	**5a** : 27%
R_1=R_2=CO_2Me [2]	**4b** : 67%	**5b** : 0%
R_1=H, R_2=SO_2Tol	**4c** : 44%	**5c** : 0%

Scheme 1.

Therefore the 1-silyl-1,4-dihydronaphthalenes **6** and **7** were prepared from 2-bromophenylacetaldehyde **8**[6] by Wittig reaction with $ICH_2P^+PH_3I^-$ 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]



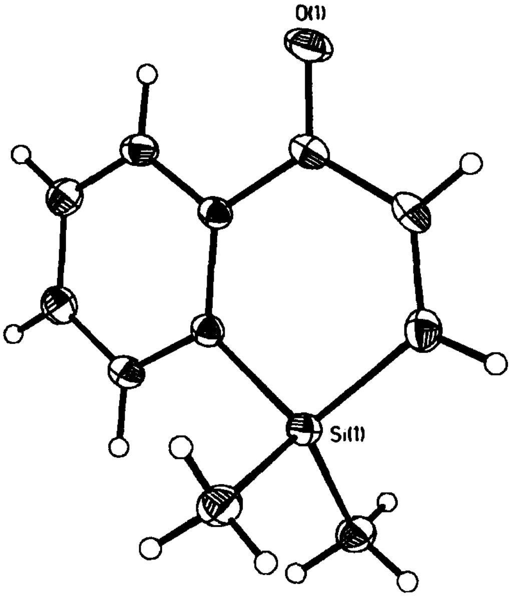
8 **9**

6 : R=Ph 50% yield
7 : R=Me 62% yield

Scheme 2.

2. Preparation of benzosilacyclohexadienones

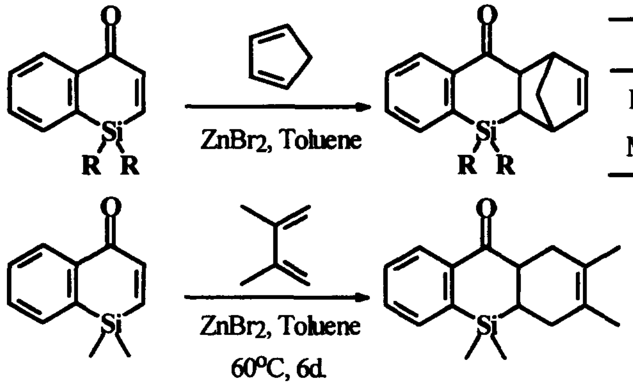
Allylic oxidation of **6** using SeO_2 in refluxing ethanol for 24 h[1a] proceeded to give a 40% yield of the benzosilacyclohexadienone **1**.[11] These conditions proved to be too harsh for substrate 7. However, the reaction of **7** with 0.5 equiv. SeO_2 in the presence of *t*-BuOOH at rt in CH_2Cl_2[12] 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 precedent[15] 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. 48–49°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]

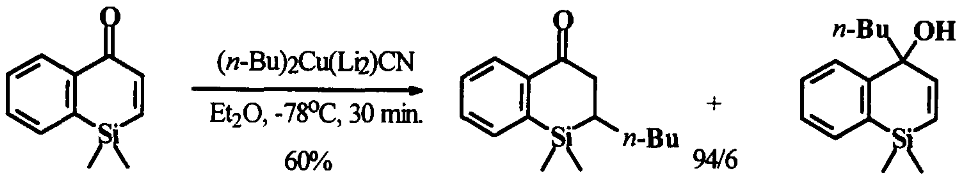


R	reaction conditions	% yield	endo/exo
Ph	reflux, 60h	0	-
Me	r.t. 17h	58	98*/2

* : compound **10**

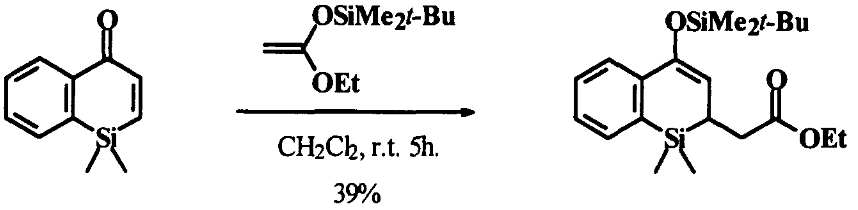
Scheme 3.

The dimethyldienone **2** undergoes conjugate addition with cyanocuprate $(n\text{-Bu})_2\text{Cu(Li)}_2\text{CN}$[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 acetal[19] 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

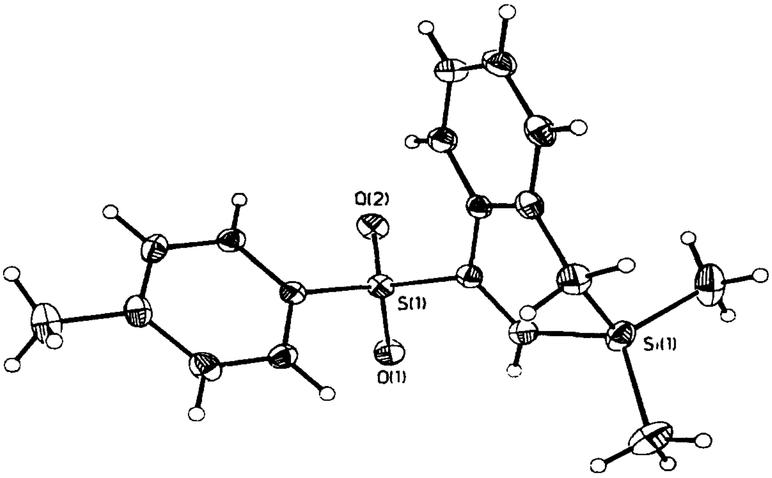
We thank the Dow Chemical Co. for a research grant to C.M.M. and Drs. W. J. Kruper and P. Nickias for helpful discussions.

References

1. (a) Barton, T. J.; Banasiak, D. S. *J. Organomet. Chem.* **1978**, *157*, 255. (b) Harada, T.; Imanaka, S.; Ohyama, Y.; Matsuda, Y.; Oku, A. *Tetrahedron Lett.* **1992**, *33*, 5807. (c) Garland, R. B.; Palmer, J. R.; Schulz, J. A.; Sollman, P. B.; Pappo, R. *Tetrahedron Lett.* **1970**, 3669. (d) Bovicelli, P.; Mincione, E.; Parsons, P. J. *Synth. Commun.* **1988**, *18*, 1231. (e) Pillot, J.-P.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1975**, 2143. (f) Felix, R. A.; Weber, W. P. *J. Org. Chem.* **1972**, *37*, 2323.
2. (a) Sakurai, H.; Imai, T. *Chemistry Lett.* **1975**, 891. (b) Takeyama, Y.; Nozaki, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1461.
3. (a) De Lucchi, O.; Modena, G. *Tetrahedron* **1984**, *40*, 2585. (b) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organometallics in Chemical Synthesis* **1970/1971**, *1*, 145. (c) Waykole, L.; Paquette, L. A. *Organic Syntheses* **1988**, *67*, 149. (d) Chen, Z.; Trudell, M. L. *Synth. Commun.* **1994**, *24*, 3149.
4. 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.

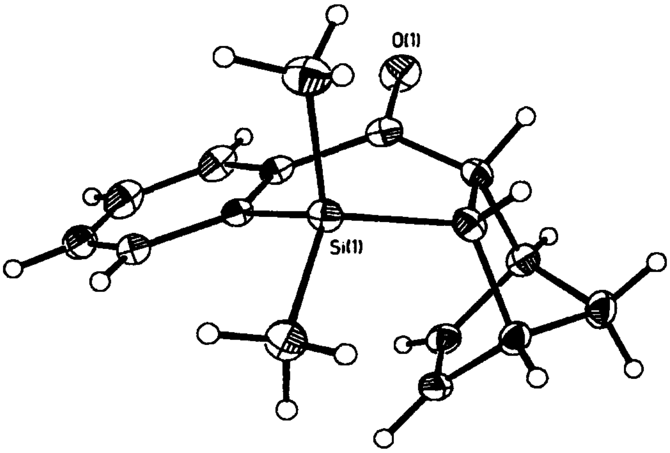
5. Compound **4c**: Monoclinic crystal system; $P2_1/c$ space group; a=16.4740(10) Å, b=8.8170(6) Å, c=11.9286(8) Å, β=95.5780(10)°; V=1724.4(2) Å^3; D(calc.)=1.265 g/mm^3; Z=4; F(000)=696; λ=0.71073 Å; T=193(2) K; crystal size=0.22×0.34×0.38 mm^3; 2.48<θ<23.27°; reflections collected: 7022, independent: 2446, observed: 2107; final R values (I>2sigmal(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$^-$/Å^3; hole: −0.281 e$^-$/Å^3.



4c

6. (a) Hartman, G. D.; Phillips, B. T.; Halcenko, W. *J. Org. Chem.* **1985**, *50*, 2423. (b) Harmata, M.; Barnes, C. L. *Tetrahedron Lett.* **1990**, *31*, 1825. (c) Hanessian, S.; Vanasse, B. *Can. J. Chem.* **1987**, 195.
7. (a) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021. (b) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 2173. (c) Bestmann, H. J.; Rippel, H. C.; Dostalek, R. *Tetrahedron Lett.* **1989**, *30*, 5261.
8. (a) Shinobuko, H.; Miki, H.; Yokoo, T.; Oshima, K.; Utimoto, K. *Tetrahedron* **1995**, *51*, 11681. (b) Maercker, A.; Bodenstedt, H.; Brandsma, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1339.
9. Compound **7**: ^{1}H NMR ($CDCl_3$, ppm): 7.51–7.10 (4H, mult.); 6.89 (1H, dt: 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). ^{13}C NMR ($CDCl_3$, ppm): 145.7; 144.2; 134.5; 133.3; 128.6; 128.3; 126.0; 125.4; 36.37; 0.96. MS (EI): 174 ($M^{+\cdot}$), 159, 143, 131. HR-MS (EI): found: 174.0859.
10. Feng, S.; Klosin, J.; Kruper, W. J.; McAdon, M. H.; Neithamer, D. R.; Nickias, P.; Patton, J. T.; Wilson, D. R.; Abboud, K. A.; Stern, C. L. *Organometallics* **1999**, *18*, 1159.
11. Compound **1**: ^{1}H NMR ($CDCl_3$, ppm): 8.28 (1H, d); 7.58–7.27 (14H, mult.); 7.15 (1H, d: J=8.7 Hz). ^{13}C NMR ($CDCl_3$, 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 ($M^{+\cdot}$), 235. HR-MS (EI): found: 312.0974.
12. Schmuff, N. R.; Trost, B. M. *J. Org. Chem.* **1983**, *48*, 1404.
13. Compound **2**: M.p.: 50–52°C; ^{1}H NMR ($CDCl_3$, 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). ^{13}C NMR ($CDCl_3$, 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, β=102.2980(10)°; V=1012.19(4) Å^3; D(calc.)=1.236 g/mm^3; Z=4; F(000)=400; λ=0.71073 Å; T=193(2) K; crystal size=0.10×0.18×0.40 mm^3; 2.56<θ<28.39°; reflections collected: 6007, independent: 2360, observed: 1963; absorption correction: SADABS; final R values (I>2sigma(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$^-$/Å^3; hole: −0.301 e$^-$/Å^3.
15. (a) Fleming, I.; Patel, S. K.; Urch, C. J. *J. Chem. Soc., Perkin Trans. 1* **1989**, 115. (b) Fleming, I.; Perry, D. A. *Tetrahedron* **1981**, *37*, 4027. (c) Fleming, I.; Patel, S. K. *Tetrahedron Lett.* **1981**, *22*, 2321.

16. Compound **10**: Orthorhombic crystal system; *Pbca* space group; a=8.13130(10) Å, b=14.18830(10) Å, c=23.8537(2) Å, β=90.0(10)°; V=2751.99(5) Å^3; D(calc.)=1.228 g/mm^3; Z=8; F(000)=1088; λ=0.71073 Å; T=193(2) K; crystal size=0.24×0.36×0.38 mm^3; 1.71<θ<28.22°; reflections collected: 15107, independent: 3280, observed: 2620; absorption coeff.=0.156 mm^{-1}; absorption correction: SADABS (empirical); final R values (I>2sigma(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$^-$/Å^3; hole: −0.394 e$^-$/Å^3.



10

17. Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, 2024.
18. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *J. Org. Chem.* **1984**, 3938.
19. (a) Rathke, M. W.; Sullivan, D. F. *Synth. Commun.* **1973**, *3*, 67. (b) Kita, Y.; Segawa, J.; Haruta, J.; Yasuda, H.; Tamura, Y. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1099.