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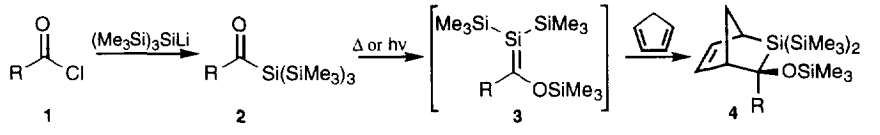
Silenes in Organic Synthesis 1: Diastereoselectivity in the Siloxysilene-Diene Diels-Alder Cycloaddition.

Andrei S. Batsanov, Ian M. Clarkson, Judith A. K. Howard[1] and Patrick G. Steel*

Department of Chemistry, Science Laboratories, University of Durham, South Road, Durham DH1 3LE

Abstract: The siloxysilene (**3**) derived from thermolysis of benzoylpolysilane undergoes a facile *in situ* cycloaddition with a range of dienes to produce the corresponding cycloadducts with modest to good diastereoselectivity. Copyright © 1996 Elsevier Science Ltd

Although the first recorded preparation of a silene appeared in 1968,[2] to date most publications have dealt with matters of structural and bonding interest with a particular focus on the preparation of stable isolable species.[3,4] In most cases these publications simply report the generation of the silene as evidenced from the results of trapping experiments with simple dienes and alcohols or through the isolation of silene dimers. Related to this report, Wiberg has studied cycloaddition reactions of symmetrical silenes, $Me_2Si{=}C(SiMe_3)_2$, with non symmetrical dienes and shown that good regioselectivity can be obtained.[5] Similarly, Auner[6] and Jones,[7] using neopentylsilenes, $R_2Si{=}CHCH_2Bu^t$, have demonstrated that moderate endo-exo ratios can be observed. However, with the exception of the relatively stable alkoxysilenes (**3**, R = a bulky group e.g. adamantyl) which have been studied by Brook and co-workers, the wider reactivity of these species remains under explored. More significantly there has been little effort to exploit the unique reactivity of these species in organic synthesis. We have initiated a programme to explore this aspect of chemistry and in this letter would like to report our preliminary results on the diastereoselectivity obtainable in the Diels-Alder reaction of phenyl(trimethylsiloxy)silene (**3**, R = Ph).



For this study we opted for the readily accessible acylpolysilanes which can be prepared through the reaction of acid chlorides with tris(trimethylsilyl)silyl lithium.[8] Photolysis of these produces the silene which, unless trapped, dimerises to afford the corresponding disilacyclobutane.[9] Whilst such a process did produce the desired cycloadduct (eg. **4**) the reaction times were long and the isolated yields low.

Subsequently, we have found that rearrangement to the silene and cycloaddition could simply and most efficiently be achieved through thermolysis. In general, heating a benzene or toluene solution of the acyl polysilane and appropriate diene at 180°C for 1-3 hours resulted in complete conversion. After cooling, the reaction mixture was concentrated and the isomer ratio (endo : exo) determined by ^{1}H NMR and glc, Table 1. The cycloadducts could be obtained pure by flash column chromatography. Only a single regioisomer could be detected whilst in no case were any products from Alder ene, [2 +2] cycloaddition or dimerisation processes isolated.

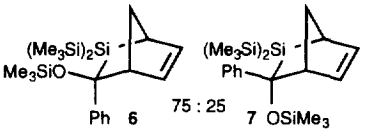
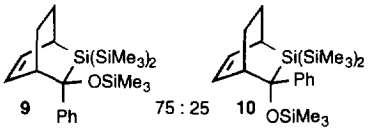
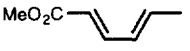
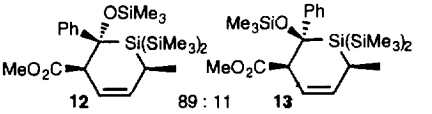
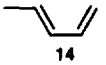
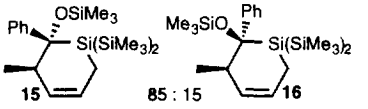
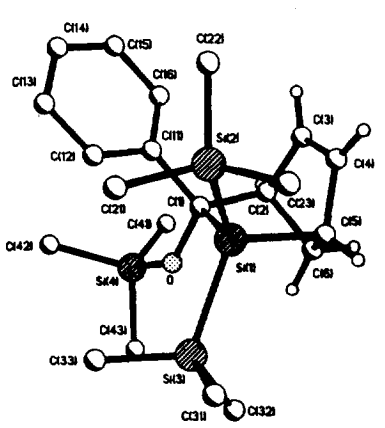
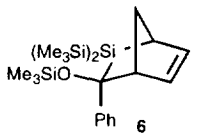
 5	Toluene 175 °C, 3h 91%	 75 : 25
 8	Toluene 180 °C, 2h 64%	 75 : 25
 11	Toluene 180 °C, 2h 57%	 89 : 11
 14	Toluene 180 °C, 2h 62%	 85 : 15

Table 1

The major isomers obtained from the reaction of cyclopentadiene and 1,3-pentadiene could be separated from the mixture by recrystallisation from hexane. Both nOe experiments and X-ray crystallography,[10] Figure 1, supported the assigned stereochemistry. Whereas the stereochemistry of the cyclopentadienyl adduct is in agreement with that previously postulated by NMR analysis, the regiochemistry of the trans piperylene adduct (**15**) is opposite to that predicted (FMO) by analogy with the reaction between isoprene and the more sterically demanding adamantyl analogue (**3**, R = adamantyl).[11] . The alkoxy silenes used in this work are less polarised than that used by Wiberg[5] in the corresponding reaction and qualitative predictions based on model calculations[12] indicate that there is negligible energy difference between the $HOMO_{(diene\text{-}\mathbf{14})}$-$LUMO_{(silene\text{-}\mathbf{3})}$ and $HOMO_{(\mathbf{3})}$-$LUMO_{(\mathbf{14})}$. Consequently, whilst the present result is consistent with a $HOMO_{(diene)}$-$LUMO_{(silene)}$ interaction with the largest orbital coefficient of the silene LUMO being located on the silicon, steric factors may well account for the difference between the phenyl and adamantyl congeners.

In conclusion, these silene cycloadditions occur in good yield, with moderate to good diastereoselectivity. Applications of the silene cycloadducts, through oxidative extrusion of silicon,[13] to lead to a 1,4 diene functionalisation protocol are currently under study and will be reported in due course.





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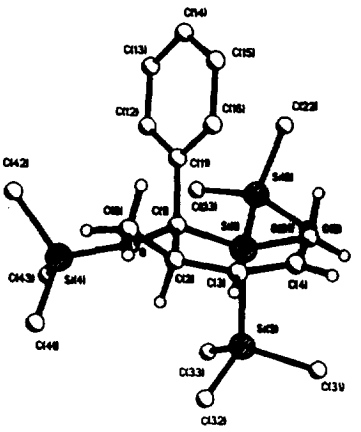

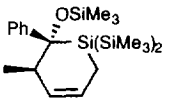

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Figure 1

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1 To whom correspondence concerning the crystal structure determinations should be addressed.

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10 Single-crystal X-ray diffraction experiments: T=150 K, Siemens SMART CCD detector, graphite-monochromated Mo-K_α radiation, λ=0.71073 Å, ω scans, semi-empirical absorption corrections (on equivalents); structure solution: direct methods; least-squares refinement: non-H atoms anisotropic, all H isotropic, against F^2 of all data (SHELXTL-PLUS software, Version 5). *Crystal data:* **6**, $C_{21}H_{38}OSi_4$, M=418.87, monoclinic, *a*=8.887(1), *b*=18.028(1), *c*=14.398(1) Å, β= 98.33(1)°, V=2539.1(5) $Å^3$, Z=4, D_c=1.10 g cm^{-3}, μ=2.4 cm^{-1}, min/max transmission (*T*) 0.843:0.953, 11338 total, 4372 unique (R_{int}=0.045) and 3152 observed ($I \geq 2\sigma(I)$) data, 387 variables, $wR(F^2)$=0.105, goodness-of-fit 1.04, R(F, observed data)=0.039, $\Delta\rho_{max}$=0.29, $\Delta\rho_{min}$=-0.25 e$Å^{-3}$; **7**, $C_{21}H_{40}OSi_4$, M=420.89, triclinic, *a*=9.014(1), *b*=9.434(1), *c*=16.804(1) Å, α=101.30(1), β=93.83(1), γ=111.61(1)°, V=1287.6(2) $Å^3$, Z=2, D_c=1.09 g cm^{-3}, μ=2.4 cm^{-1}, *T* min/max 0.882:0.952, 5870 total, 4172 unique (R_{int}=0.026) and 3762 observed data, 395 variables, $wR(F^2)$=0.100, goodness-of-fit 1.10, R(F, obs. data)=0.035, $\Delta\rho_{max}$=0.32, $\Delta\rho_{min}$=-0.23 e$Å^{-3}$. Atomic coordinates, bond distances and angles have been deposited at the Cambridge Crystallographic Data Centre.

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