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Silene Stereochemistry. 3. The Configurational Stability of 1-Methyl-1-phenyl-2-neopentylsilene

Paul Ronald Jones* and Myong Euy Lee

Department of Chemistry, North Texas State University
Denton, Texas 76203-5068

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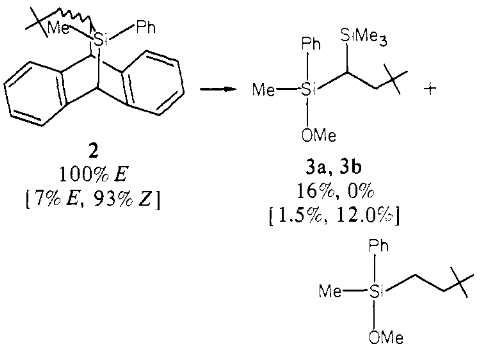
In 1979 Sakurai and co-workers reported evidence that 2,3-diphenyl-2,3-disila-2-butene is configurationally stable toward cis–trans isomerization at temperatures up to 350 °C.[1] More recently Brook and co-workers observed for a series of 1,1-bis(trimethylsilyl)-2-trimethylsiloxysilenes generated by photolysis of tris(trimethylsilyl)acylsilanes four distinct ^{29}Si resonances at temperatures up to 60 °C, indicating that there is no free rotation about the Si–C bond in these highly crowded silenes at least up to that temperature.[2] We recently reported evidence indicating that 1-methyl-1-phenyl-2-neopentylsilene (**1**) generated by the reaction of *tert*-butyllithium with vinylmethylphenylchlorosilane is configurationally stable at or below room temperature.[3] We now wish to present the first evidence that a silene, **1**, is configurationally stable up to 300 °C.

When pure (*E*)-2-methyl-2-phenyl-3-neopentyl[5,6:7,8]dibenzo-2-silabicyclo[2.2.2]octane[3] (*E*-**2**) is subjected to sealed tube thermolysis[4] at 300 °C for 10 h in the presence of 20 mol % excess of trimethylmethoxysilane, 37% decomposition (based on recovered anthracene) of the starting material occurred. A 16% yield of *one* diastereomer, **3a**, the trimethylmethoxysilane adduct to the silene **1**,[5] and a 67% yield of 5,5-dimethyl-2-methoxy-2-phenyl-2-silahexane (**4**),[6] along with traces of the silene dimers,[7] were obtained. No isomerization of the recovered starting material (63%) had occurred. When a mixture of 7% *E*-**2** and 93% *Z*-**2** were thermolyzed under identical conditions 39% decomposition occurred to give a 13.5% yield of a mixture of the diastereomers **3**, consisting of 90% of the diastereomer **3b**,[8] presumably arising from the reaction of *Z*-**1** with trimethylmethoxysilane, and a 49% yield of **4**. The recovered starting material (61%) consisted of 10% of the *E* and 90% of the *Z* isomer.



2
100% *E*
[7% *E*, 93% *Z*]

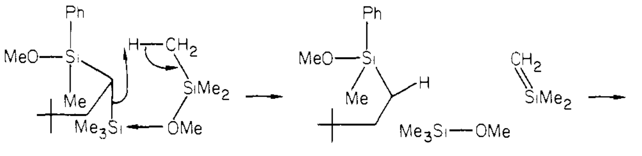
3a, **3b**
16%, 0%
[1.5%, 12.0%]

4
67%
[49%]

recovered **2**
100% *E*
[10% *E*, 90% *Z*]

In the absence of trimethylmethoxysilane and thermolysis of **2** gives typical silene products.[9] The percent decomposition of the anthracene adducts **2** is independent of the concentration of trimethylmethoxysilane over a concentration range from a 5- to a 30-fold excess of the trap. These observations indicate that free silene is being produced and that the diastereomers **3** do not arise through a bimolecular reaction between **2** and the trapping reagent.

Compound **4**, an unexpected product, has been shown to arise from a secondary reaction between the α-(trimethylsilyl)methoxysilane **3** and trimethylmethoxysilane. When a 62:38 mixture of **3a** to **3b** was subjected to sealed-tube pyrolysis at 300 °C for 20 h in the presence of a 20 mol % excess of trimethylmethoxysilane, a 75% yield of **4** was obtained, while the ratio of **3a** to **3b** in the recovered starting material had not changed. This indicates that this secondary reaction does not perturb the stereochemical results. In addition, [(trimethylsilyl)methyl]methoxydimethylsilane (**5**) the product of the reaction of dimethylsilene with trimethylmethoxysilane[10] was observed in the product mixtures. In the absence of trimethylmethoxysilane **3a** and **3b** are stable under the pyrolysis conditions. A possible pathway for the formation of **4** could involve an electrocyclic reaction between **3** and the trimethylmethoxysilane.



3

4

$Me_3SiCH_2SiMe_2OMe$

5

Trimethylmethoxysilane has been shown to be an efficient, regiospecific silene trap.[10] Our results show that its reaction with silenes is also stereospecific. It might be reasonable to assume that the cycloreversion leading to the (*E*)- or (*Z*)-silene **1** is concerted and stereospecific [4s + 2s] reaction.[11] However, for our system the determination of stereochemistry of the silene generation reaction and the trapping reaction hinges on the determination of the actual configurations of the two diastereomers **3a** and **3b**, which we are actively pursuing.

Nevertheless, the fact that *E*-**2** gives only **3a** and *Z*-**2** gives predominantly **3b** with less than 1% isomerization indicates unambiguously that 1-methyl-1-phenyl-2-neopentylsilene is configurationally stable at temperatures up to 300 °C.

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(4) In typical experiments weighed samples of the silene precursor, *E*- or *Z*-**2**, combined with a 20 mol % excess of trimethylmethoxysilane and hexadecane as an internal standard in cyclohexane solvent were degassed and sealed in 7 mm × 12 cm Pyrex tubes under vacuum. The entire tube was then placed in a vertical pyrolysis oven that was preheated to the temperature indicated. Analysis of the product mixtures was accomplished by a capillary (25-m fused silica SE-54) column and FID detection, and yields were calculated by an internal standard method. All new products gave satisfactory elemental analyses.

(5) MS of both **3a** and **3b**, *m/e* (relative intensity) 293 (19) P – 15, 251 (14) P – *t*-Bu, 203 (4) $PhCH_2Si{=}CH$*t*-Bu^+, 151 (100) $PhMeSiOMe^+$, 147 (36) $PhMeSi{=}CH_2^+$, 135 (19), 121 (44) $PhMeSiH^+$, 89 (12) Me_2SiOMe^+, 85 (14), 73 (23) $SiMe_3^+$, 59 (18) Me_2SiH^+, 57 (6) *t*-Bu^+; ^{1}H NMR of **3a** (chemical shifts are in ppm downfield from Me_4Si) 0.02 (s, 9 H), 0.41 (s, 3 H), 0.67 (s, 9 H), 3.37 (s, 3 H), 0.05–0.09 (m, 1 H), 1.42–1.52 (m, 2H), 7.22–7.57 (m, 5 H); ^{13}C NMR of **3a** (chemical shift in ppm downfield from Me_4Si) (multiplicity of off-resonance ^{1}H-decoupled signal) –3.64 (q, SiMe), 0.40 (q, $SiMe_3$), 8.85 (d, CH=), 29.59 (q, $C(CH_3)_3$), 31.61 (s, $C(CH_3)_3$), 36.94 (t, CH_2), 50.60 (q, $SiOCH_3$), 127.59 (d), 129.09 (d), 134.10 (d), 138.78 (s, aryl carbons).

(6) MS of **4**, *m/e* (relative intensity) 221 (3) P – 15, 158 (14), 151 (100) $PhMeSiOMe^+$, 137 (19) $PhMeSiOH^+$, 121 (64) $PhMeSiH^+$, 105 (15), 91 (25), 75 (5) $MeHSiOMe^+$, 59 (32) Me_2SiH^+, 57 (7) *t*-Bu^+; ^{1}H NMR of **4** 0.12 (s, 3 H), 0.34–0.59 (m, 2 H), 0.63 (s, 9 H), 0.92–1.23 (m, 2 H), 3.18 (s, 3 H), 6.97–7.54 (m, 5 H); ^{13}C NMR of **4** –4.36 (q, SiMe), 9.17 (m, $SiCH_2$), 28.87 (q, $C(CH_3)_3$), 31.08 (s, $C(CH_3)_3$), 36.94 (m, $CH_2C(CH_3)_3$), 50.85 (q, SiOMe).

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(8) ^{1}H NMR of **3b** –0.03 (s, 9 H), 0.43 (s, 3 H), 0.72 (s, 9 H), 3.33 (s, 3 H), 0.05–0.10 (m, 1 H), 1.42–1.52 (m, 2 H), 7.20–7.60 (m, 5 H); ^{13}C NMR of **3b** –2.92 (q, SiMe), 0.01 (q, $SiMe_3$), 9.24 (d, CH=), 29.59 (q, $C(CH_3)_3$), 31.61 (s, $C(CH_3)_3$), 36.94 (t, CH_2); 50.40 (q, SiOMe), 127.59 (d), 129.09 (d), 134.42 (d), 137.98 (s, aryl carbons).

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In similar thermolysis studies carried out at 370 °C, we have observed 12–15% isomerization of the *E* and *Z* isomers of 1. When *E*- or *Z*-**1** is generated under flash-vacuum pyrolysis conditions at 550 °C, complete randomization of stereochemistry occurs and identical product mixtures are obtained for either isomer.[12]

We are currently carrying out carefully controlled thermolyses at a series of temperatures aimed at determining the activation energy (and thus the Si=C π bond energy) for the isomerization.

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Diels–Alder Reactions of Fischer Carbene Complexes

William D. Wulff* and Dominic C. Yang

Searle Chemistry Laboratory, Department of Chemistry
The University of Chicago, Chicago, Illinois 60637

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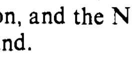
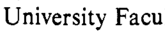
The heteroatom-stabilized carbene complexes of the group 6 transition metals (Fischer carbene complexes[1]) were the first to be prepared[2] and are among the most stable of all transition-metal carbene complexes.[3] The chemical and physical properties of these complexes have been interpreted in terms of a polarized chromium–carbon bond with the carbon bearing an appreciable positive charge.[4,5] An example is the tremendous thermodynamic acidity of the α protons ($pK_a \simeq 8$) in the complex **1**.[6] With this



pKa≅8

1

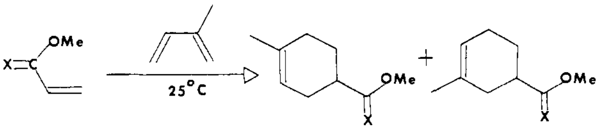


δ=323 ppm

5

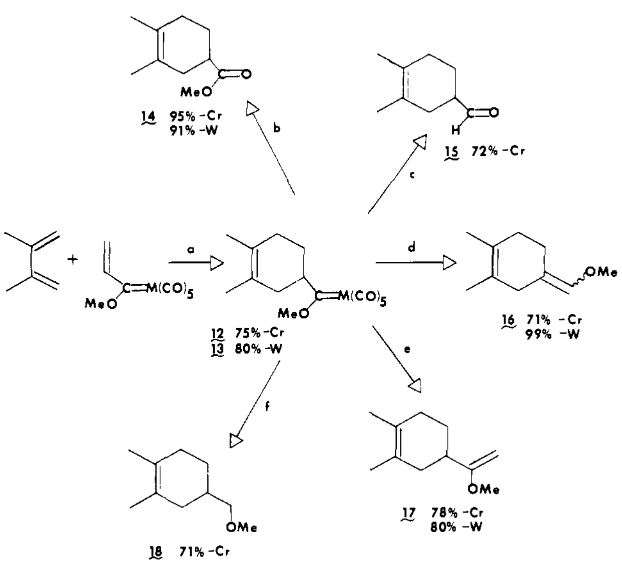
in mind and in an effort to find alternatives to or synthons for the Diels–Alder reaction, we were led to examine the dienophilicity of α,β-unsaturated complexes such as **5**.[7]

The vinyl-substituted complexes **5**–**7**[8] react with a variety of dienes with rate accelerations of greater than 10^4 over that of methyl acrylate, their closest carbon analogue. The comparative data for isoprene is presented in Table I. Methyl acrylate has previously been observed to react with isoprene in 7 months at 25 °C to give a 54% yield of a 70:30 mixture of the "para" and "meta" isomers **8** and **9**.[9] The chromium complex **5** on the other hand, reacts in 3 h at 25 °C to give after chromatographic purification on silica gel with hexane a 70% yield of **8** and **9** as a 92:8 mixture. A ratio of the rate constants gives a rate enhancement of 2.1 x 10^4, and as can be anticipated there is an associated increase in the regioselectivity. It is interesting to note that the increased reactivities in the reaction of these complexes with isoprene are comparable to those of the aluminum chloride catalyzed reaction of methyl acrylate and isoprene.[10]



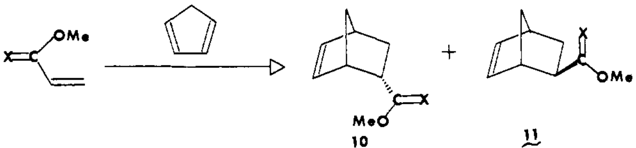
8 **9**

Scheme I



^{a} (a) C_6H_6, 25 °C, 1.5 h; (b) Me_2SO, 3.5 h, 25 °C; (c) 10^{-3} M in CH_2Cl_2, 1 equiv of HBr, −78 → 25 °C, 1 equiv of HBr, −78 → 25 °C; (d) 1.1 equiv of pyridine, THF ⇅, 5 h; (e) excess CH_2N_2 in Et_2O, 25 °C, 5 min; (f) 69 atm H_2/hexane, 170 °C, 48 h.

The vinyl-substituted complexes **5** and **7** have been found to react with cyclopentadiene in a highly stereoselective fashion in accord with the Alder endo rule (Table II). The red vinyl chromium complex **5** reacts with cyclopentadiene in 3 min at 25 °C to give a 78% yield of the yellow endo and exo cycloadducts **10** and **11** in a ratio of 94:6 that is identical with the endo/exo ratio obtained from the aluminum chloride catalyzed reaction of methyl acrylate and cyclopentadiene.[11] Given the substantial acidity of protons α to the carbene carbon in Fischer carbene complexes,[6] we have taken a mixture of **10** and **11** (X = W(CO)$_5$) that is enriched in the exo isomer **11** (5.1:1.0) and found that the composition of the mixture is unaffected by either exposure to the reaction conditions or by oxidation to the corresponding methyl esters. This indicates that the endo/exo ratios given in Table II represent kinetic values.



10 **11**

These metal-complexed cycloadducts can serve as synthons for a variety of organic functional groups by employing known reactions of Fischer carbene complexes.[12] We have examined a few of these methods for the chromium and tungsten adducts **12** and **13** (Scheme I). Esters can be obtained with a variety of oxidizing agents of which the mildest is perhaps dimethyl sulf-

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