

THE SYNTHESIS OF 1-BENZYLDIMETHYLSILYL-4-PHENYLTHIO-1,3-BUTADIENE:  
 A NEW DIENE-REGENERABLE DIELS-ALDER SYNTHON

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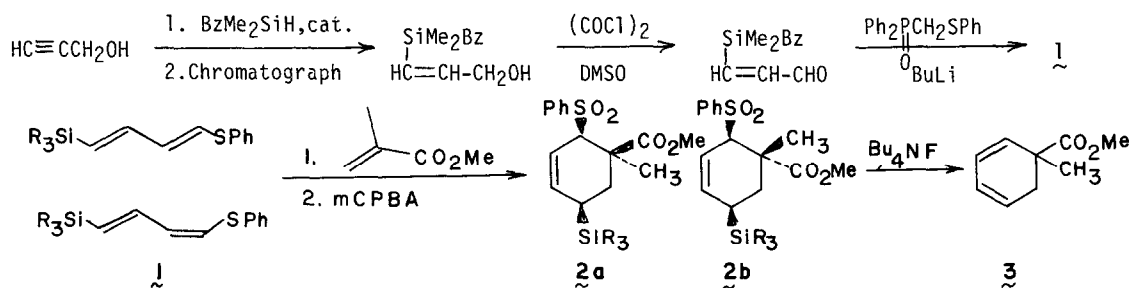
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Summary: 1-Benzyl dimethylsilyl-4-phenylthio-1,3-butadiene (**1**), prepared by hydrosilylation of propargyl alcohol, oxidation and followed by Wittig-Horner reaction, underwent Diels-Alder reaction with methyl methacrylate. The adduct after oxidation to the sulfone when treated with fluoride gave 5-carbomethoxy-5-methyl-1,3-cyclohexadiene.

Many natural products such as occidentol<sup>1,3</sup>, damascenone<sup>2</sup> and the germacranolides<sup>3</sup> contain or might be derived from the 1,3-cyclohexadiene functionality. Therefore it would be useful to devise a 1,3-butadiene which after an initial 4+2 cycloaddition would give an adduct that could be readily converted to a 1,3-cyclohexadiene.<sup>4</sup>

1-Benzyl dimethylsilyl-4-phenylthio-1,3-butadiene (**1**) was prepared in three steps: hydrosilylation of propargyl alcohol, oxidation to the silylpropargaldehyde and Wittig-Horner reaction using (phenylthiomethyl)diphenylphosphine oxide. The hydrosilylation was accomplished by adding a catalytic amount (18mg, 0.04 mole %) of oxygenobis(triphenylphosphine)platinum(II) to a 1:1 solution of propargyl alcohol (63 mmol) and benzyl dimethylsilane (63 mmol) under nitrogen and heating at 110° for 4h. After bulb to bulb distillation, 124-134°(1mm), the isomers were separated on 230-240 mesh silica gel eluting with 40% ether-pentane to give a 30% yield of 3-benzyl dimethylsilyl-2-propen-1-ol and 23% of the 2-isomer. Dimethylphenylsilane gave substantially the same results, but trimethylsilane gave principally the corresponding silyl ethers.

The 3-benzyl dimethylsilyl-2-propen-1-ol was oxidized to the aldehyde with oxalyl chloride-dimethylsulfoxide in methylene chloride in 97% yield. The silyl aldehyde in THF at room temp-



perature was added to diphenyl(phenylthiomethyl)phosphine oxide<sup>6</sup> resulting in a 95% yield of the (E,E) and (E,Z) dienes (1) in a 3:1 ratio. The mixture (1) was subjected to Diels-Alder reaction with, for example, methyl methacrylate in a sealed tube at 150° for 48h giving an 82% yield (based on diene consumed) of 3-phenylthio-6-benzylidimethylsilyl-4-carbomethoxy-4-methylcyclohexene. This product was oxidized using m-chloroperbenzoic acid<sup>7</sup> yielding (80%) a 1.2:1 mixture of isomeric sulfones (2ab). The isomeric sulfones were separated by chromatography and their structures assigned by their 500MHz NMR spectra<sup>8</sup> with extensive decoupling experiments. The regiochemistry of the Diels-Alder addition is indicated by the multiplicity of H-3 and H-6 because H-6 is clearly coupled to H-5 and H-5'. Coupling constants  $J_{2,3}$  and  $J_{1,6}$  indicate that the benzenesulfonyl group is pseudo-axial and that the trialkylsilyl group is pseudo-equatorial. A syn-diaxial interaction with the 4-methyl or 4-carbomethoxy group prevents the silyl group being axial. The two isomeric sulfones 2a and 2b differ in the stereochemical relationship of the 4-methyl and 4-carbomethoxy groups. Treatment of 2ab with tetra-n-butylammonium fluoride in THF<sup>9</sup> lead to facile 1,4-elimination giving a quantitative yield of 5-carbomethoxy-5-methylcyclohexa-1,3-diene (3).<sup>10</sup>

Two other dienophiles were used with the diene 1. Dimethyl maleate was heated in a 1:1 mixture with 1 for 12h at 160° resulting in a 50% yield of adduct. 4-Phenyl-1,2,4-triazolinedione (0.17g, 1mmol) with 1 (0.3g, 1mmol) in ether solution (25mL) at 25° for 2h resulted in 20% recovered 1 and a 74% yield of adduct.

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8. 2a <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.8-6.9 (m, 10H, aryl), 5.94 (dd, 1H, J 10, 1.7 Hz, H-1), 5.28 (ddd, 1H, J 10, 5.8, 2.8 Hz, H-2), 3.83 (d, 1H, J 5.8 Hz, H-3), 3.68 (s, 3H, OCH<sub>3</sub>), 2.36 (dd, 1H, J 15, 11.5, Hz, H-5), 2.12 (d, 1H, J 14 Hz, SiCH<sub>2</sub>Ph), 2.08 (d, 1H, J 14 Hz, SiCH<sub>2</sub>Ph), 1.66 (dd, 1H, J 15, 6.6, Hz, H-5'), 1.59 (m, 1H, J 11.5, 6.6, 2.8, 1.7 Hz, H-6), 1.16 (s, 3H, C-CH<sub>3</sub>), -0.0428 (s, 3H, SiCH<sub>3</sub>), -0.0498 (s, 3H, SiCH<sub>3</sub>).
- 2b <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.95-6.97 (m, 10H, aryl), 5.81 (dd, 1H, J 10, 2.4 Hz, H-1), 4.84 (m, 1H, J 9.9, 5.6, 2.7 Hz, H-2), 4.31 (d, 1H, J 5.6 Hz, H-3), 3.59 (s, 3H, OCH<sub>3</sub>), 2.41 (dd, 1H, J 13.9, 11.1 Hz, H-5), 2.19 (d, 1H, J 13.8 Hz, SiCH<sub>2</sub>Ph), 2.09 (d, 1H, J 13.8 Hz, SiCH<sub>2</sub>Ph), 2.02 (dd, 1H, J 13.9, 6.8 Hz, H-5'), 1.74 (m, 1H, J 11.1, 6.8, 2.7, 2.4 Hz, H-6), 1.63 (s, 3H, C-CH<sub>3</sub>), -0.0003 (s, 3H, SiCH<sub>3</sub>), -0.0235 (s, 3H, SiCH<sub>3</sub>).
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10. 3 <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.74-5.98 (m, 4H, vinyl), 2.79 (ddd, 1H, J 18, 3.8, 2.0 Hz, H-6'), 2.24 (ddd, 1H, J 18, 4.7, 1.5 Hz, H-6), 1.60 (s, 3H, C-CH<sub>3</sub>); M.s. m/z (M<sup>+</sup>) Calcd. 152.0837, obsd. 152.0822.

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