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2-Trimethylsilylvinylboranes: Highly Reactive and Selective Diels-Alder Equivalents of 2-Trimethylsilylvinyl Alcohol and Acetylene

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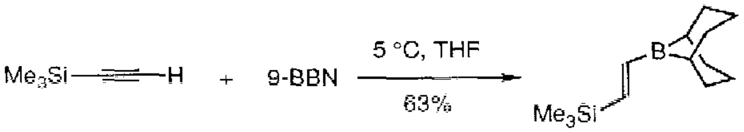
Summary: The readily available 2-trimethylsilylvinyl-9-BBN (**1**) is a highly reactive and selective dienophile. The Diels-Alder products are easily converted into trimethylsilylcyclohexenols and 1,4-cyclohexadienes.

Due to the low reactivity of acetylene in Diels-Alder reactions, many ingenious dienophilic acetylene equivalents have been developed.[1-3] However, several of these synthons are so unreactive that they are useless with all but the most reactive dienes, and an additional number would generally require prohibitively vigorous reaction conditions with complex acyclic dienes. Of the more reactive acetylene equivalents, 1,2-bis(phenylsulfonyl)ethylenes and related compounds have seen most common use in recent years,[4] but the final elimination step with these dienophiles is often inefficient. 2-Phenylsulfonylnitroethylene has shown considerable promise due to its higher reactivity and the gentle conditions (Bu_3SnH) for the final elimination,[2] but has seen little use, possibly owing to its more difficult availability. A number of efficient intramolecular transition-metal catalyzed [4+2] cycloadditions of alkynes are known,[5] but the corresponding intermolecular reactions are subject to a number of problems and lack generality.[5b]

We have recently reported that vinyldialkylboranes are exceptionally reactive, regioselective, and *endo*-stereoselective Diels-Alder dienophiles.[6] The special activating properties of a dialkylboron group and the synthetic versatility of the products should allow the development of a variety of new boron-activated dienophiles which solve synthetic problems. We were interested in applying vinylborane chemistry in the development of a dienophilic equivalent of acetylene. We report here the excellent utility of 2-trimethylsilylvinylboranes as synthetic equivalents of 2-trimethylsilylvinyl alcohol and acetylene.

Hydroboration of trimethylsilylacetylene with 9-BBN in the absence of solvent has recently been reported to afford only a 9% yield of 2-trimethylsilylvinyl-9-BBN (**1**).[7] In contrast, we have been able to obtain pure **1** in 63% yield by reacting 9-BBN with 1.5 equiv of trimethylsilylacetylene in a dilute (≈0.1 M) solution in THF for 4 d at 5 °C, followed by distillation of the reaction mixture [bp 60 °C (0.005 mm)]. Compound **1** is highly air-sensitive and pyrophoric but is considerably more stable than unsubstituted vinylboranes and can be kept at room temperature for weeks without noticeable decomposition.



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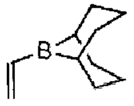

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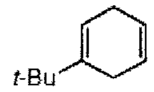
Surprisingly, **1** is only slightly less reactive than the parent vinyl-9-BBN (**2**). The rate constant for reaction of **1** with cyclopentadiene was $3.5 \times 10^{-5}\ M^{-1}s^{-1}$ at 25 °C compared to a rate constant of $6.5 \times 10^{-5}\ M^{-1}s^{-1}$ at 25 °C for the reaction of **2**. In contrast, while nitroethylene has been reported to react with cyclopentadiene at -100 °C,[8] 2-trimethylsilylnitroethylene utilizes refluxing benzene![9] Acyclic dienes react especially fast with **1**; 2-*tert*-butylbutadiene is more reactive ($k = 8.2 \times 10^{-5}\ M^{-1}s^{-1}$ at 25 °C) than cyclopentadiene with **1**, but is ≈40 times less reactive with maleic anhydride.[10] Reactions of **1** with butadiene and isoprene proceed to completion within a day at 40-50 °C. Amazingly, **1** appears to be considerably more reactive than 2-phenylsulfonylnitroethylene with such simple acyclic dienes, based on reported reaction conditions.[2] In all of the reactions of **1**, the formation of the Diels-Alder adduct appears to be quantitative by NMR before workup. Oxidation of the adducts with H_2O_2/NaOH afforded the silyl alcohols **3**-**10** in good yield (Table 1).[11,12]

Steric effects apparently play a large role in determining the regiochemical outcome of these reactions. The regioselectivity observed in the reaction of isoprene with **1** was higher than had been observed with either 3-trimethylsilylacrylic acid (50:50)[3] or 2-trimethylsilylnitroethylene (75:25),[9] but much greater selectivity still (>98%) was obtained in the reaction of 2-*tert*-butylbutadiene with **1**. Models suggest that steric interaction of the *tert*-butyl group with the bulky BBN group would occur in a transition state leading to the disfavored "meta" isomer.

The regioselectivity and *endo*-stereoselectivity observed in the reaction of **1** with *trans*-piperylene were most striking. The presence of the trimethylsilyl group results in increased *endo*-stereoselectivity; no *exo* product could be observed by either ^{13}C NMR, 400 MHz ^1H NMR, or GC. However, the major regioisomer is *reversed* from that observed with **2**, which had afforded only *meta* substituted products.[6] These surprising results were carefully confirmed by ^1H NMR decoupling experiments in both cases. The reaction of piperylene is notably slower than the reaction of butadiene, so both the formation of **6** and **7** must be hindered, but a detailed explanation of the preference for **6** is lacking. Padwa has observed a similar reversal of regiochemistry in 1,3-dipolar cycloadditions on adding a trimethylsilyl group to a dipolarophile.[13] As had been observed with **2**, much lower *endo*-stereoselectivity is observed in the reaction of **1** with the cyclic diene cyclopentadiene.

Treatment of neat samples of the purified silyl alcohols derived from 2-*tert*-butylbutadiene, butadiene, isoprene, and *trans*-piperylene with ≈1 mol % p-toluenesulfonic acid, followed by gentle warming to 55 °C for 5-60 min, afforded the 1,4-cyclohexadienes **11**, **12**, **13**, and **14** respectively, quantitatively and cleanly by GC and ^1H and ^{13}C NMR.[14] Unfortunately, a complex mixture of products was produced when the mixture of cyclopentadiene-derived alcohols **8** and **9** were reacted under these conditions. We are currently searching for satisfactory reaction conditions for the formation of norbornadiene.



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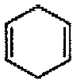

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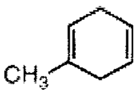

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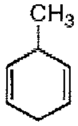

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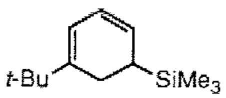

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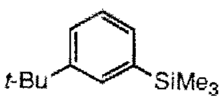

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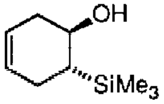
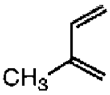
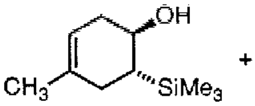
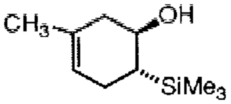
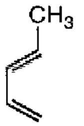
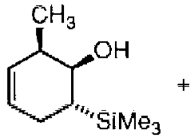
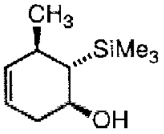
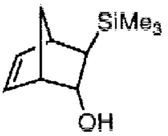
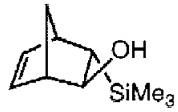
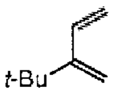
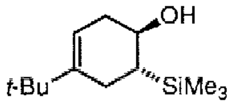
The utility of the Diels-Alder adducts of **1** is further demonstrated by their conversion to 5-trimethylsilyl-1,3-cyclohexadienes. Treatment of the adduct of **1** and 2-*tert*-butylbutadiene with six equiv of acetaldehyde at 57 °C overnight afforded after chromatography a 78% yield of **15** contaminated by ≈10% **16**. In the presence of oxygen, the slow conversion of **15** to **16** was observed. 5-Trimethylsilyl-1,3-cyclohexadienes should be versatile substrates for electrophilic substitutions.

Table 1. Reaction Conditions, Products, and Yields for Diels-Alder Reactions with **1**.

Diene	Rxn Conditions	Product(s) and Ratio	% Yield[a]
	22 h, 50 °C	 **3**	85
	24 h, 45 °C	 +  **4** 85:15 **5**	73
	144 h, 85 °C	 +  **6** 88:12 **7**	63
	20 h, 25 °C	 +  **8** 3:1 **9**	87
	11 h, 25 °C	 **10**[b]	87

[a]Isolated, unoptimized. [b]>98% one regioisomer.

The ready availability of **1**, its high reactivity with simple acyclic dienes, and the simplicity and efficiency of the transformation of the adducts into 1,4-cyclohexadienes should make **1** widely attractive as an acetylene equivalent in Diels-Alder reactions. The utility of **1** should be particularly useful in reactions of complex acyclic dienes. Application of the versatility of organoborane chemistry to the Diels-Alder adducts of **1** should make it an effective synthetic equivalent of many other dienophiles, including unactivated trimethylsilylalkenes and trimethylsilylketene. We plan to continue developing diverse dienophiles which exploit the unique properties of vinylboranes in Diels-Alder reactions.

Acknowledgment. We thank The Robert A. Welch Foundation and the Texas Advanced Research Program for support of this research.

References and Footnotes

(1) For examples, see: Kumar, P. R. *J. Chem. Soc., Chem. Commun.* **1989**, 509. Paquette, L. A.; Moerck,

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(4) See De Lucchi, O.; Fabbri, D.; Cossu, S.; Valle, G. *J. Org. Chem.* **1991**, *56*, 1888, and references therein.

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(9) Hayama, T.; Tomoda, S.; Takeuchi, Y.; Nomura, Y. *J. Org. Chem.* **1984**, *49*, 3235.

(10) Craig, D.; Shipman, J. J.; Fowler, R. B. *J. Am. Chem. Soc.* **1961**, *83*, 2885.

(11) In a typical procedure, a mixture of 1.085 g (20.1 mmol) of butadiene and 0.965 g (4.38 mmol) of **1** was heated to 50 °C for 22 h in a sealed tube. Removal of the butadiene under vacuum afforded the borane adduct as a clear liquid with no impurities detectable by ^{1}H or ^{13}C NMR. The borane was diluted with 10 mL of THF, cooled to 0 °C, and sequentially 1.46 mL of 3 N NaOH and 1.31 mL of 30% H_2O_2 were added. The mixture was stirred at 25 °C for 90 min, diluted with 50 mL of water, and extracted with 100 mL and 50 mL portions of 30-60° petroleum ether. The combined extracts were made basic by addition of five drops of triethylamine, dried (Na_2SO_4), and the solvent was removed on a rotary evaporator. The residue was chromatographed on a 12" x 5/8" flash silica gel column using 1% triethylamine and 11% ethyl acetate in 30-60° petroleum ether as eluent to afford 635 mg (85%) of **3** as a white crystalline solid: mp 41-44 °C.

(12) The regiochemistry of **4** was established by ^{1}H NMR decoupling experiments, which indicated that the carbinol proton of **4** was coupled to two adjacent methylene protons, one of which was coupled by 5.1 Hz to the vinylic proton. An analogous coupling constant of 4.8 Hz was observed in **10**. The stereochemistry of **6** was assigned from coupling constants of the carbinol proton with the methine protons adjacent to the methyl and silyl groups of 4.5 and 8.0 Hz, respectively. The stereochemistry of **9** was assigned from the presence of *W*-coupling between carbinol and *anti*-C_7 protons.

(13) Padwa, A.; Wannamaker, M. W. *Tetrahedron* **1990**, *46*, 1145.

(14) We were unable to cleanly separate **12**-**14** from hexamethyldisiloxane on the small scales employed. Compound **11** was obtained free of the byproduct hexamethyldisiloxane by evaporative distillation at 50 mm, albeit with some loss (75% yield). The isolated **11** was contaminated with small amounts of the corresponding aromatic when oxygen was present during the procedure.

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