applicablility to vibrational assignments of systems where there is extensive hydrogen bonding.

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Efficient Entry to Tetrahydropyridines: Addition of Enol Ethers to Allenesulfonamides Involving a Novel 1,3-Sulfonyl Shift**

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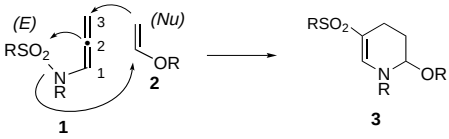
Owing to the ground-state strain and the allylic stabilization of the resultant carbanion, allenes bearing electron-withdrawing substituents (W) are highly reactive toward nucleophilic addition at the central sp carbon atom [Eq. (a)].[1] Nucleophilic addition to the terminal sp^2 carbon atom of

(a)

allenes, on the other hand, takes place with difficulty[2] owing to the lack of a substituent to stabilize the developing anionic charge on the central carbon atom.[3] Here we report that enol ethers **2** assist *N*-allenesulfonamides **1** to undergo a novel 1,3-shift of the sulfonyl group and eventually furnish tetrahydropyridines **3** in good to excellent yields [Eq. (b)]. The reaction



(b)

is triggered most likely by nucleophilic attack of **2** at the terminal carbon atom of the allenic C2–C3 double bond, activated through space by the nearby sulfonyl group ($\pi^*_{C-C3} - \sigma^*_{N-S}$ interaction).

As reported recently from our laboratories,[4] 4-vinylidene-1,3-oxazolidin-2-one **1a**, when heated with electron-deficient or conjugated alkenes (e.g., styrene, 1,3-butadienes) at 70–100 °C, undergoes a facile [2+2] cycloaddition reaction via a concerted $[\pi_{2s}+\pi_{2s}+\pi_{2s}]$ Hückel transition state to provide cyclobutane derivatives **4** in excellent yields. For example, **1a** reacts with methyl acrylate (**2a**) to provide **4a**, which can be isolated in 73% yield (Scheme 1). We were pleasantly surprised to find that methyl β-methoxyacrylate ((*E*)-**2b**) reacted in a completely different manner than **2a** (Scheme 1): When a mixture of **1a** (0.5 mmol) and (*E*)-**2b** (20 mmol) was

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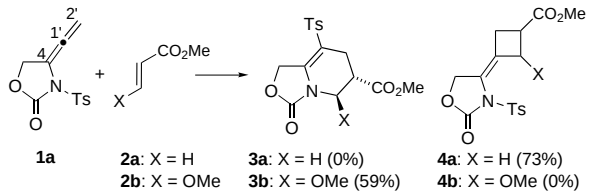


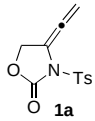
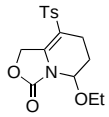
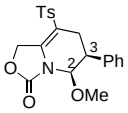
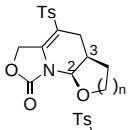
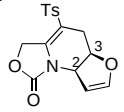
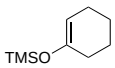
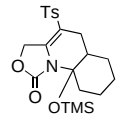
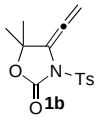
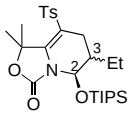
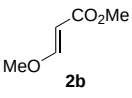
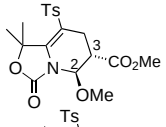
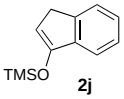
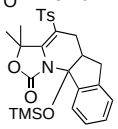
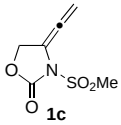
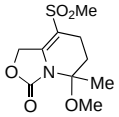
Scheme 1. Reaction of **1a** with electron-deficient alkenes.

heated at 70 °C for 23 h under N_2, **1a** underwent a unique skeletal rearrangement to selectively provide bicyclic tetrahydropyridine derivative *trans*-**3b** (isolated in 59% yield). The expected [2+2] addition product **4b** was not detected at all. The formation of *trans*-**3b** apparently indicates that N–SO_2 bond cleavage and migration of the sulfonyl group from nitrogen to carbon C1′ (1,3-sulfonyl shift) take place.

As summarized in Table 1, enol ethers, encompassing acyclic (**2b–d**, **2i**) and cyclic aldehyde enol ethers (**2e–g**) as well as acyclic (**2k**) and cyclic keto-enol ethers (**2h**, **2j**), all behaved in a similar manner and provided **3** exclusively. All the products were characterized by IR, ^{1}H NMR (400 MHz), and ^{13}C NMR spectroscopy (100 MHz), high-resolution mass spectrometry, and/or elemental analyses. The structures of **3f** and **3j** were determined unequivocally by X-ray crystallographic analyses, which revealed that the alkoxy substituents at C2 occupy a quasi-axial position of the tetrahydropyridine ring in order to avoid steric and electrostatic repulsions with the carbonyl oxygen atom of the oxazolidinone unit).

Among the results in Table 1, the following points deserve comment: First, it is known that furan tends to act as a 4π component and undergo Diels–Alder reaction with allenes.[5] However, in the present reaction it served as a dienol ether. It reacted presumably as a nucleophile at the 2-position to give **3g** selectively (run 5), a regioisomer that differs from the other compounds **3** with respect to the position of the oxygen atom on the tetrahydropyridine ring (C3-O for **3g**, otherwise C2-O). Second, despite severe repulsion[6] between the oxazolidinone carbonyl moiety and C2 substituents, geminally C2-disubstituted **3** (e.g., **3h**, **3k**, and **3l**) are obtained in excellent yields. Finally, the reaction is highly stereoselective, providing the products with retention of configuration of the starting alkenes: (*Z*)-**2d** (*E*:*Z* = 1:17) gave *cis*-**3d** exclusively (run 2). The C2–OMe_{ax}/C3–$phenyl_{eq}$ structure was deduced from the 400-MHz ^{1}H NMR spectrum ($^3J(C2H_{eq}–C3H_{ax}) = 2.2$, $^3J(C3H_{ax}–C4H_{eq}) = 13.4$, $^3J(C3H_{ax}–C4H_{eq}) = 3.7$ Hz), and large increments in the area intensity of $C2H_{eq}$ (14%) and $C4H_{eq}$ (11%) by irradiation of the signal for $C3H_{ax}$.[7] Similarly, (*E*)-**2b** (*E*:*Z* > 99:1) gave rise to *trans*-**3b** (Scheme 1) and *trans*-**3j** (run 8 and Figure 1) exclusively. In contrast, lower stereoselectivity was observed for the reaction of (*Z*)-**2i** (*E*:*Z* = 1:10, run 7), where a mixture of *cis*-**3i** and *trans*-**3i** in a ratio of 4:1 resulted. No epimerization at C2 of **3i** was observed during purification of the reaction mixture by column chromatography over silica gel.

Table 1. Novel addition–cyclization reaction of 4-vinylidene-1,3-oxazolidin-2-ones **1a–c** and enol ethers **2**.

Run	1	2	Reaction conditions[a] *T*[°C]/*t*[h]	Products (yield[%])[b]
1	 **1a**	 **2c**	100/8	 **3c** (92)
2	**1a**	 **2d**	80/24	 **3d** (75)
3	**1a**	 **2e** (n = 1) **2f** (n = 2)	100/24 80/12	 **3e**, n = 1 (75) **3f**, n = 2 (89)
5	**1a**	 **2g**	80/48	 **3g** (60)
6	**1a**	 **2h**	70/6	 **3h** (88)[c]
7	 **1b**	 **2i**	80/33	 **3i** (90)[d]
8	**1b**	 **2b**	70/15	 **3j** (72)
9	**1b**	 **2j**	80/85	 **3k** (66)
10	 **1c**	 **2k**	70/45	 **3l** (74)

[a] A mixture of **1** (0.5 mmol) and **2** [**2b** (10 mmol, *E*:*Z* > 99:1), **2c** (50 mmol in 1 mL of dioxane), **2d** (10 mmol, *E*:*Z* = 1:17; recovered **2d**: *E*:*Z* = 1.3:1), **2e** (40 mmol in 1 mL of dioxane), **2f** (10 mmol in 1 mL of dioxane), **2g** (10 mmol in 1 mL of dioxane in a sealed tube), **2h** (5 mmol in 0.4 mL of dioxane), **2i** (5 mmol, *E*:*Z* = 1:10, in 1 mL of dioxane; recovered **2i**: *E*:*Z* = 1:2), **2j** (10 mmol), or **2k** (40 mmol in 0.5 mL of dioxane)] was heated under N_2. [b] Yields of isolated spectroscopically homogeneous **3**. [c] Combined yield of isolated **3h** (59%) and its desilylated OH derivative (29%). [d] *trans*-**3i**:*cis*-**3i** = 1:4.

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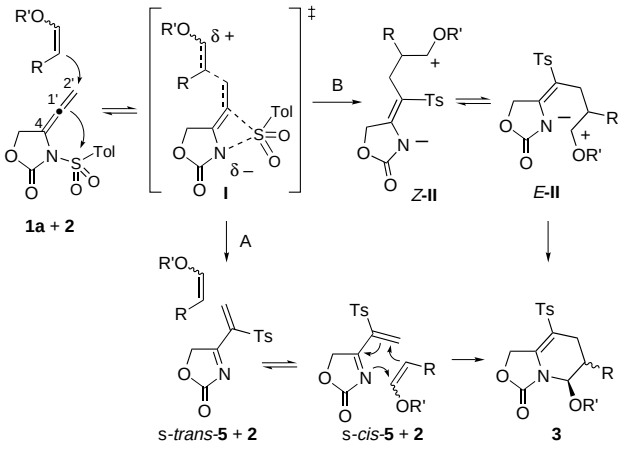
Two reasonable pathways accounting for the selective formation of **3** are shown in Scheme 2.[8] In the transition state **I**, electron density is pushed into the sulfonamide moiety through the C1′–C2′ double bond, and the N–S bond is weakened. At the same time, electron density is drawn away from the carbamate by conjugation through the C4–C1′ double bond. This allows the 1,3-sulfonyl shift[9, 10] and hence the isomerization of **1a** to s-*trans*-1-azabutadiene **5** (path A). Compound **2** is itself restored by $E-Z$ isomerization. Indeed, **2d** and **2i** isomerized during the reaction with **1**, and were



Scheme 2. Two possible pathways for the selective formation of tetrahydropyridines **3**.

recovered as mixtures with E:Z ratios of 1.3:1 (run 2) and 1:2 (run 7), respectively. In the absence of **1**, no isomerization of **2d** and **2i** was observed. In the absence of **2**, **1b** remained intact and was recovered quantitatively (in dioxane at 80 °C, 24 h). In contrast, **1a** readily isomerized even at 60 °C and gave 3-tosyl-4-vinyl-4-oxazolin-2-one (by a 1,3-H shift) in varying yields (15–50%, in dioxane, 10 h)[11] and decomposed completely at 80 °C (24 h) to give an intractable tarry mixture. Thus, **1** promotes the isomerization of **2**, and **2** stimulates the 1,3-sulfonyl shift of **1** (to give intermediate **5**[12]) rather than the 1,3-H shift. The thus-formed **5** is expected to be highly reactive toward hetero-Diels–Alder reaction with enol ethers[13] and would readily react with (*Z*)-**2** (rather than with (*E*)-**2**, probably owing to steric reasons) to furnish *cis*-2,3-disubstituted **3**[14] either exclusively (run 2) or selectively (run 7).

Path B might contribute to some extent, especially for the reactions with enol ethers (e.g., ketone enol ethers and furans[15]) that are highly electron-donating and able to stabilize zwitterionic species of type **II**.

In conclusion, we have demonstrated that allenesulfonamides **1a–c** undergo a novel cyclization reaction with a variety of enol ethers **2** to provide bi-, tri-, and tetracyclic tetrahydropyridines **3** in good to excellent yields. The reaction most likely proceeds by an enol ether promoted isomerization of **1** to **5**, which then undergoes hetero-Diels–Alder reaction with **2** (see Scheme 2). Reactions of **1** with electron-rich alkenes (enamines, allylsilanes, allylstannanes) and soft Lewis bases (phosphanes, low-valent transition metals) are under intensive study.

Experimental Section

Run 8 from Table 1: A mixture of **1b** (0.5 mmol, $R_f = 0.57$, hexane/ethyl acetate 2/1 v/v)[4] and **2b** (10 mmol, E:$Z > 99$:1, Aldrich) was heated at 70 °C for 15 h under N_2, after which excess **2b** was removed in vacuo. The resultant sticky mixture was purified by column chromatography over silica gel (hexane/ethyl acetate 4/1 v/v) and then recrystallized from CH_2Cl_2/hexane to give **3j** in 72% yield: $R_f = 0.63$ (hexane/ethyl acetate 2/1 v/v); m.p. 193.0–193.5 °C; IR (KBr): $\tilde{\nu} = 1800$ (s), 1720 (s), 1640 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 1.94$ (s, 3H), 1.99 (s, 3H), 2.45 (s, 3H), 2.52 (dd, $J = 5.7$, 16.5 Hz, 1H, $C4H_{ax}$), 2.66 (ddd, $J = 1.1$, 2.2, 16.5 Hz, 1H, $C4H_{eq}$), 2.99 (dt, $J = 5.7$, 2.2 Hz, 1H, $C3H_{eq}$), 3.42 (s, 3H), 3.45 (s, 3H), 5.39 (dd, $J = 1.1$, 2.2 Hz, 1H, $C2H_{eq}$), 7.35 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.4$ Hz, 2H); correct elemental analysis (C,H,N,S).

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[7] Similar coupling patterns and nOes were observed for *cis*-**3f** and *cis*-**3i**. See the Experimental Section for the characteristic coupling patterns that *trans*-**3** displays.

[8] A radical mechanism involving homolytic N–S bond cleavage may be ruled out based on the fact that methanesulfonamide **1c** (run 10, Table 1) shows reaction features similar to those of toluenesulfonamides **1a**, **b**: B. Quiclet-Sire, S. Z. Zard, *J. Am. Chem. Soc.* **1996**, *118*, 1209–1210; S. Kim, J.-Y. Yoon, *J. Am. Chem. Soc.* **1997**, *119*, 5982–5983, and references therein.

[9] A similar four-membered cyclic transition state has been proposed for the 1,3-shift of chlorine in chlorocarbonylketene: J. Finnerty, J.

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Andraos, Y. Yamamoto, M. W. Wong, C. Wentrup, *J. Am. Chem. Soc.* **1998**, *120*, 1701 – 1704.; see also H. Bibas, M. W. Wong, C. Wentrup, *Chem. Eur. J.* **1997**, *3*, 237 – 248, and references therein.

[10] To the best of our knowledge, this is the first example for the displacement of nitrogen from sulfonamide by a nucleophilic carbon atom. For displacement of nitrogen by a nucleophilic oxygen atom, see D. L. Comins, A. Dehghani, *Tetrahedron Lett.* **1992**, *33*, 6299 – 6302; Z. Xu, X. Lu, *Tetrahedron Lett.* **1997**, 38, 3461 – 3464. The sulfonamide N–SO_2 bond is so strong that it must be cleaved under rather harsh conditions: D. J. Ramon, G. Guillena, D. Seebach, *Helv. Chim. Acta* **1996**, *79*, 875 – 894. Other modifications of N–SO_2 bond cleavage: S. M. Weinreb, D. M. Demko, T. A. Lessen, *Tetrahedron Lett.* **1986**, *27*, 2099 – 2102; T. Fukuyama, C.-K. Jow, M. Cheung, *Tetrahedron Lett.* **1995**, *36*, 6373 – 6374; C. Huart, L. Ghosez, *Angew. Chem.* **1997**, *109*, 627 – 629; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 634 – 636.

[11] Thiophene failed to react with **1a** to furnish **3**. Instead, 4-vinyl-4-oxazolin-2-one (product of a 1,3-hydrogen shift) was provided in 88 % yield (**1a**/thiophene = 1/100 mol/mol, 80 °C, 11 h).

[12] No trace of **5** was detected when run 8 of Table 1 was monitored by ^{1}H NMR spectroscopy and HPLC. There were only very small amounts of impurities; 20, 29, and 51 % conversions after 2, 4, and 9 h at 70 °C, respectively.

[13] D. L. Boger in *Comprehensive Organic Synthesis*, *Vol. 5* (Eds.: B. M. Trost, I. Fleming, L. A. Paquette), Pergamon, Oxford, **1991**, pp. 470 – 507; L. F. Tietze, G. Kettschau, *Top. Curr. Chem.* **1997**, *189*, 1 – 120.

[14] T. Bando, H. Harayama, Y. Fukazawa, M. Shiro, K. Fugami, S. Tanaka, Y. Tamaru, *J. Org. Chem.* **1994**, *59*, 1465 – 1474.

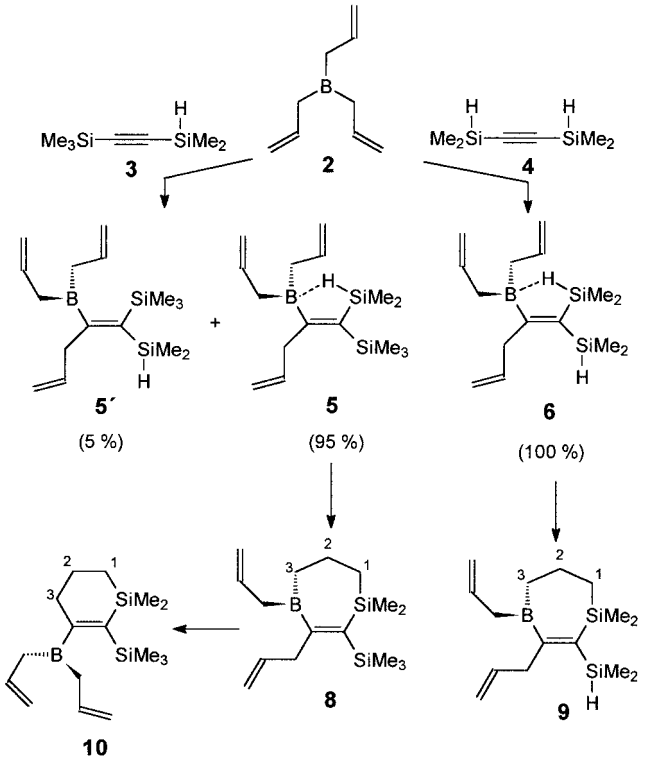
[15] We thank the referee who pointed out the possibility that **3g** might be formed by the Diels – Alder addition of furan (4π) and the vinyl group of **5** and subsequent 1-aza-Cope rearrangement.

The First Si-H-B Bridge: Combination of 1,1-Organoboration and Hydrosilylation**

Bernd Wrackmeyer,* Oleg L. Tok, and Yuri N. Bubnov

The enormous synthetic potential of organoboron[1] and organosilicon compounds[2] is well documented. However, the combination of reactive species from both areas has not been studied extensively.[3–6] 1-Alkynylsilanes are known to react with diorganoboron hydrides by 1,2-hydroboration[4] and also by cleavage of the Si–C_{sp} bond, depending on the reaction conditions.[5] 1,1-Organoboration of 1-alkynylsilanes takes place if they are treated with triorganoboranes such as triethylborane (**1**) and heated up to 100 °C.[3c, 6] Boron compounds containing silyl groups with Si–H functionalities have received even less attention so far.

We have now observed that the reaction conditions for 1,1-organoboration can be much milder (room temperature, 0.5 – 1 h) if triallylborane (**2**), instead of **1**, and 1-alkynylsilanes with Si–H bonds, for example dimethylsilyl(trimethylsilyl)-ethyne (**3**) and bis(dimethylsilyl)ethyne (**4**), are used. In the reaction products, the mutual positions of silyl and boryl groups at the C=C bond rouses in particular two questions: 1) Does the presence of the neighboring three-coordinate boron atom induce Si–H bond activation, or in other words, is there a Si-H-B bridge? 2) Are there further reactions between the Si–H functionalities and the C=C double bonds of the allyl groups? The answer to both questions is yes, as shown in Scheme 1.



Scheme 1. Reactions of triallylborane **2** with the 1-alykynylsilanes **3** and **4**.

The spectroscopic data of all compounds discussed here are summarized in Table 1. The presence of a Si-H-B bridge in **5** and **6** is reflected unequivocally by ^{1}H, ^{11}B, and ^{29}Si NMR and IR spectroscopic data. The ^{1}H NMR signal of the hydrogen atom in the bridge is broad, it is shifted to high field by about 1.5 ppm with respect to resonances for "normal" Si–H groups (for example, the second Me_2SiH group in **6**), and it is shifted further to high field at lower temperature (–30 °C; $\Delta\delta = -0.3$). The ^{11}B nuclear shielding is increased by about 20 (**6**) or 30 ppm (**5**) when compared with derivatives without a Si-H-B bridge. The ^{29}Si nuclear shielding is decreased by 34 (**6**; Figure 1) or 44 ppm (**5**) already at room temperature, and it decreases further at lower temperature (**5** (–30 °C): δ^{29}Si =

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