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Novel 1,3-sulfonyl shift and [4+2] cycloaddition reaction of *N*-allenyl sulfonamide promoted by allylsilane

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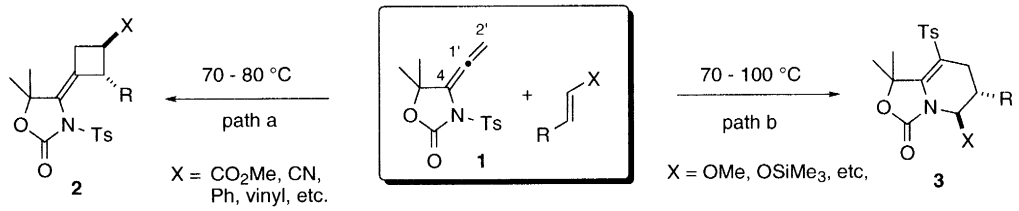
Abstract

The thermal reaction of allylsilanes and 5,5-dimethyl-3-tosyl-4-vinylidene-1,3-oxazolidin-2-one (**1**) at 80–100°C selectively furnishes tetrahydropyridine derivatives **5**. The reaction involves a novel 1,3-sulfonyl shift as the key step.

Keywords: allenes; cycloadditions; rearrangements; silicon and compounds.

Recently, we have reported that 5,5-dimethyl-3-tosyl-4-vinylidene-1,3-oxazolidin-2-one (**1**) and its derivatives undergo a facile [2+2] cycloaddition reaction with alkenes bearing a variety of electron-withdrawing and π-conjugating substituents under strictly thermal conditions at 70–80°C (path a, Scheme 1).[1] The reaction displays high stereospecificity and regioselectivity and furnishes methylene-cyclobutane derivatives **2** in excellent yield. In sharp contrast to this, under similar conditions, electron-rich alkenes such as enol ethers of aldehyde, ketone, and ester, induce a novel skeletal rearrangement of **1** to selectively furnish tetrahydropyridine derivatives **3** in excellent isolated yield (path b, Scheme 1).[2]



Scheme 1.

In Scheme 2 is outlined one of the most probable reaction pathways proposed for the reaction of **1** and enol ethers, which invokes a novel N→C1′ 1,3-sulfonyl group rearrangement. The rearrangement is

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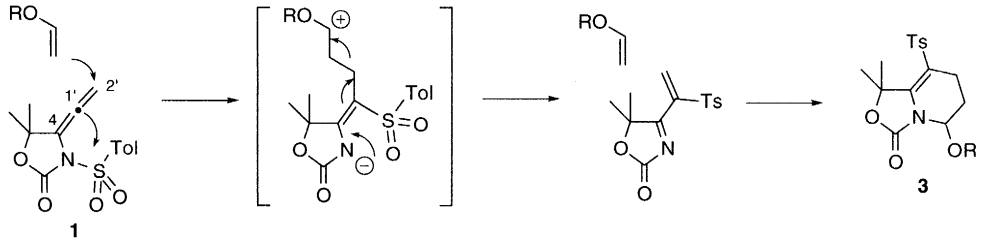
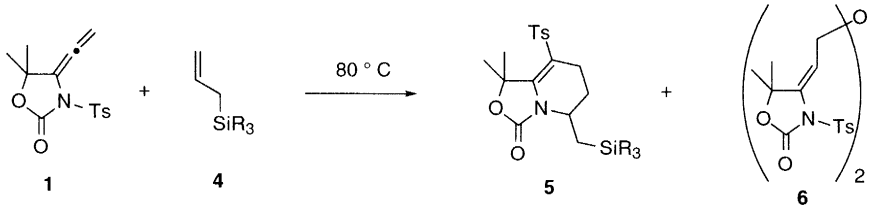
triggered by the nucleophilic attack of enol ethers to the terminal C2′ position of the allene double bond of **1**.[2]



Scheme 2.

In order to shed more light on the mechanistic aspects of this unprecedented rearrangement, we examined the reaction by using allylsilanes as a probe. Allylsilanes are a rather poor nucleophile as compared to enol ethers, yet they belong to a unique class of compounds, the double bonds of which display versatile nucleophilic reactivity; they serve not only as an allylating agent of carbonyl compounds,[3] but also as a 2- and 3-carbon component for the [2+2] and [2+3] cycloaddition reaction with compounds possessing polarized C=C double bonds.[4]



(1)

Here we would like to report that allylsilanes react with **1** with ease, similar to enol ethers, and serve nicely as a 2-carbon component for the formal [4+2] cycloaddition to selectively provide tetrahydropyridines **5** (Eq. (1)). Thus, when allyltrimethylsilane (**4a**: R=Me, 5 mmol) and **1** (0.5 mmol) were heated in dry dioxane (1 ml) at 80°C (bath temperature) under nitrogen, **5** and **6** appeared at the expense of **1** as monitored by TLC (run 1, Table 1). After separation by column chromatography over silica gel and recrystallization from dichloromethane–hexane, **5** and **6** were obtained as colorless crystals in 56 and 20% yield, respectively. The structures of these products were fully characterized by ^{1}H, ^{13}C NMR, IR, and elemental analyses[5] and were determined unequivocally by X-ray crystallographic analyses[6] (Fig. 1). The reaction was invariably accompanied with bis-allyl ether **6** as a minor product; however, the origin of the ether oxygen atom of **6** and the reaction pathway leading to **6** are not clear at present.

The reaction feature of allylsilanes **4** depends markedly on the kind of the substituent R: **4b** (R=isopropyl) and **4c** (R=Ph) react in a way similar to **4a** (R=Me) and furnish mixtures of **5** and **6**, while **4d** (R=OEt) and **4e** (R=Cl) are definitely unreactive. During extended heating with **4d** or **4e**, **1** decomposed to give an intractable mixture of products that did not contain **5** (TLC monitoring).

The reaction feature also has turned out to depend significantly on the structure of the allylic moiety of **4**. 2-methylallyl(trimethyl)silane (**4f**) reacted with **1** as usual and provided a mixture of a [4+2] cycloaddition product **5f** and bis-allyl ether **6** in 57 and 10% yield, respectively (Eq. (2)), while 2-phenylallyl(trimethyl)silane (**4g**) reacted with **1** to give a [2+2] cycloaddition product **7** in good yield (Eq. (3)). A thorough examination of the reaction mixture detected no [4+2] cyclization product, indicating that the styrene moiety of **4f** is more influential than the allylsilane moiety to determine the reaction course (Scheme 1).[1]

Table 1
Thermal cycloaddition reaction of allylsilanes **4** toward 5,5-dimethyl-3-tosyl-4-vinylidene-1,3-oxazolidin-2-one (**1**)[a]

run	allylsilane **4**	temp (°C)	time (h)	% isolated yield of **5** and **6**	
1	**4a**: R = Me	80	25	**5a**: 56	**6**: 20
2	**4b**: R = i-Pr	80	12	**5b**: 48	**6**: 19
3	**4c**: R = Ph	80	10	**5c**: 40	**6**: 10
4	**4d**: R = OEt	80	24	**5d**: 0[b]	**6**: ---[d]
5	**4e**: R = Cl	80	48	**5e**: 0[c]	**6**: ---[d]

a) General reaction conditions: **1** (0.5 mmol) and **4** (5 mmol) in dry dioxane (1 ml) under nitrogen. For the structures of **1**, **4**, **5**, and **6**, see equation 1. b) Complete decomposition of **1**. c) Partial decomposition of **1**. d) No attempt has been made to isolate **6**.

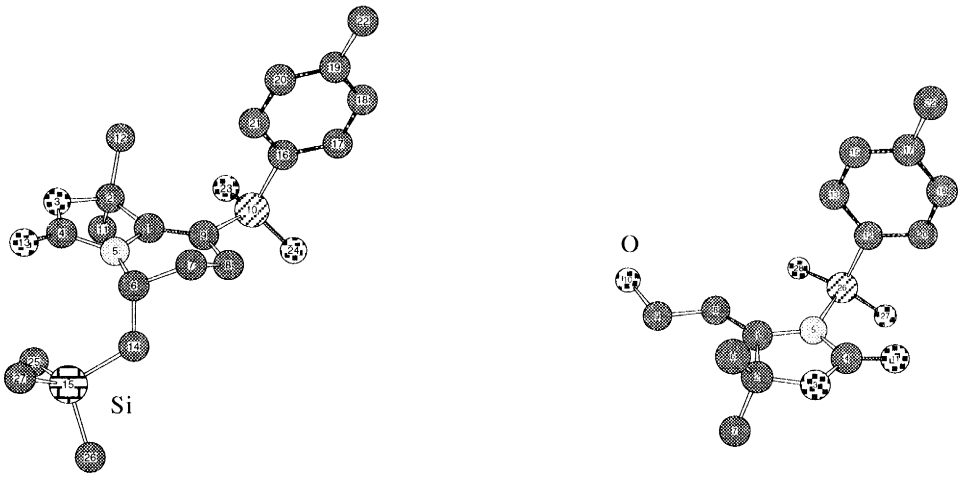
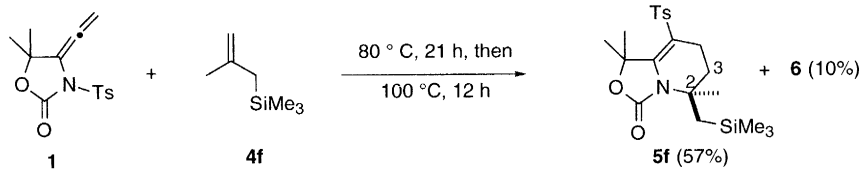
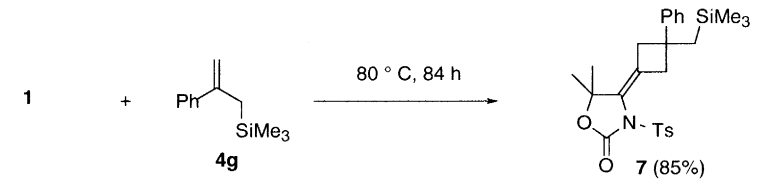


Fig. 1. Chem 3D™ perspective views of the crystal structures of **5a** (left) and **6** (right, only the right-half is shown). For simplicity, all hydrogens are omitted



(2)



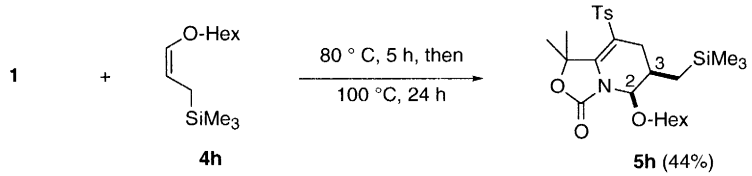
(3)

It may be worth noting that the relative reactivity order observed here (**4b**, **4c**>**4a**>**4f**, estimated on the basis of the reaction time required to complete the reaction) seems to be inversely correlated to 'the scales of nucleophilicity', proposed by Mayr et al. (**4f**≫**4a**, **4b**>**4c**).[7] Furthermore, surprisingly, even though they are expected to be by far more reactive as a nucleophile than allylsilanes **4**, allylstannanes turned out to be very reluctant to undergo cycloaddition reaction with **1**. Thus, **1** was recovered almost

completely when a mixture of **1** (0.5 mmol) and allyl(tributyl)stannane (5 mmol) in dioxane (1 ml) was heated at 80°C for 10–15 h under nitrogen.

These results, as well as the comparative reactivity of allylsilanes and enol ethers (vide supra), suggest that some factors other than nucleophilicity, such as Lewis acidity of allylsilanes, operate to accelerate the reaction of allylsilanes toward **1**. That is, the silicon of allylsilanes might coordinate to the sulfonamide oxygen to increase the leaving ability of the sulfonyl group.

Bearing this idea in mind, we examined the reaction of (*Z*)-3-hexyloxylallyl(trimethyl)silane (**4h**) and **1** (Eq. (4)) in an expectation that an intramolecular coordination of the silicon of **4h** to its ether oxygen might inhibit an intermolecular coordination of the silicon to the sulfonamide oxygen of **1**, and hence might retard the [4+2] cycloaddition reaction. Indeed, almost no reaction was observed when the mixture of **1** and **4h** was heated under the usual conditions (80°C, 5 h). For the reaction to proceed at a reasonable rate, a higher temperature was required (100°C, 24 h).



(4)

The reaction also displayed some interesting features of the regio- and stereoselectivity: **4h** reacted with **1** to provide a cycloaddition product **5h** with a completely opposite regioselectivity, locating a trimethylsilylmethyl group at the C3 position of the tetrahydropyridine ring. This result clearly indicates that the enol ether moiety of **4h** is more influential than the allylsilane moiety for determining the orientation in the Diels–Alder reaction (Scheme 2).[2] As to the stereoselectivity, the *cis*-geometry of **4h** was retained in the product *cis*-**5h**.[8] The structure of *cis*-**5h** was determined on the basis of NOE experiments.

In summary, allylsilanes reacted with *N*-allenyl sulfonamide **1** under strictly thermal conditions at 80–100°C and selectively provided tetrahydropyridine derivatives **5**. The reaction involves a novel 1,3-sulfonyl rearrangement of **1** as the key step. The characteristic reactivity of allylsilanes, serving not only as a nucleophile but also as a Lewis acid, seems to play a crucial role in promoting the 1,3-sulfonyl rearrangement. Further study aimed at clarification of the mechanism for the rearrangement and of the pathway for the formation of bis-allyl ether **6** is in progress.

Acknowledgements

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2. Horino, Y.; Kimura, M.; Wakamiya, Y.; Okajima, T.; Tamaru, Y. *Angew. Chem., Int. Ed. Engl*. **1999,** *38*, 121–123.
3. Yamamoto, Y.; Asao, N. *Chem. Rev*. **1993**, *93*, 2207–2293.
4. Knolker, H.-J. *J. prakt. Chem*. **1997**, *339*, 304–314. In most cases, these reactions are promoted only in the presence of some Lewis acid catalysts.

5. 6-Aza-5-(trimethylsilylmethyl)-9,9-dimethyl-2-tosyl-8-oxabicyclo[4.3.0]non-1-en-7-one (**5a**): mp=173.0–173.5°C (CH_2Cl_2/hexane); IR (KBr) 2950 (w), 1770 (s), 1630 (s), 1390 (m), 1370 (m), 1320 (m), 1290 (s), 1240 (m), 1160 (m), 1140 (s), 1090 (m), 1070 (w) 1060 (w), 960 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9 H), 0.69 (dd, *J*=10.3, 14.5 Hz, 1H), 0.94 (dm, *J*=14.5 Hz, 1H), 1.57 (dm, *J*=13.6 Hz, 1H), 1.80 (dm, *J*=13.6 Hz, 1H), 1.94 (s, 3H), 1.98 (s, 3H), 2.15 (dm, *J*=16.7 Hz, 1H), 2.30 (dm, *J*=16.7 Hz, 1H), 2.45 (s, 3H), 4.20 (br. quint, *J*=4.2 Hz, 1H), 7.34 (d, *J*=8.2 Hz, 2H), 7.73 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.1, 19.8, 21.3, 21.6, 25.1, 26.3, 26.7, 47.3, 86.4, 106.1, 127.3, 129.8, 137.9, 144.0, 149.7, 153.4; HRMS calcd for: $C_{20}H_{21}O_4NSSi$: 407.1587; found *m/z* (relative intensity): 407.1595 (M^+, 100), 91 (7), 73 (41). Anal. calcd for $C_{20}H_{21}O_4NSSi$: C, 58.94; H, 7.17; N, 3.44; found: C, 58.57; H,7.03; N, 3.42.
6. The authors have deposited atomic coordinates for **5a** and **6** (deposition nos. CCDC-139284/139285) with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre 23 Union Road, Cambridge, CB2 1EZ, UK.
7. (a) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 984–947. (b) Burfeindt, J.; Patz, M.; Muller, M.; Mayr, H. *J. Am. Chem. Soc*. **1998**, *120*, 3629–3634.
8. (*Z*)-**4h** isomerized during the reaction and (*Z*)-**4h**/(*E*)-**4h**=3.7:1 was recovered from the reaction mixture.