Hydrozirconation of Allenyl Sulfide for Generating γ-Thio-substituted Allylzirconium Species and Its Reaction with Carbonyl Compounds

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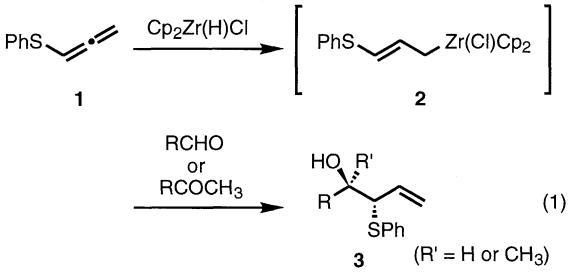
Hydrozirconation of allenyl sulfide generates a γ-thio-allylzirconocene species, which reacts with aldehydes and ketones to give anti olefinic β-sulfenyl alcohols in highly regio- and stereoselective manner.

γ-Thio-substituted allylmetals **A** are among the versatile classes of organosulfur reagents in organic synthesis.[1,2] Based on our previous finding on the accessibility to various *allylzirconocene species via the hydrozirconation of allenes*,[3] we envisioned to generate the Zr-version of **A** [M = $Cp_2Zr(Cl)$-] by applying the above protocol to thio allene **B**.

Figure 1.

A **B**

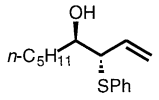
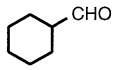
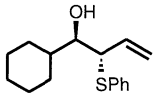
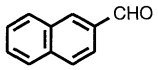
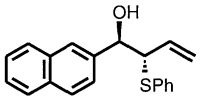
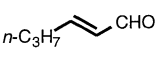
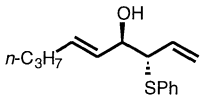
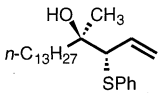
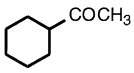
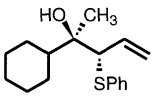
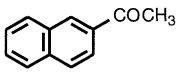
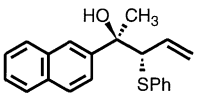
In this communication, we wish to report the viability of such an approach to γ-thioallylzirconocene chloride **2** and the reaction with carbonyl compounds to give olefinic β-sulfenyl alcohols **3** in high stereoselectivity (Eq. 1).



Allenyl sulfide **1**[4] underwent clean hydrozirconation by a similar procedure we previously reported,[3] and the resulting thioallylzirconium **2** smoothly reacted with aldehydes at –78 °C. The addition proceeded with high stereoselectivity to give the *anti*-adducts in high yield, as had been the case for various other allylzirconiums (Table 1).[3,5,6] The addition to α,β-unsaturated aldehyde proceeded in a 1,2-mode to give **3d**, and none of the 1,4-adduct was observed (run 4). The olefinic β-sulfenyl alcohols, thus obtained in high stereoselectivity, were easily converted to vinyl epoxides, which served to confirm the stereostructure of the major adducts.[6] Furthermore, at the temperature of 0 °C, the thioallylzirconium **2** proved to react with ketones to give high yields of the adducts **3e–3g**.[5,7] In case the sterics of the two substituents attached to the ketone carbonyl were sufficiently different, good to high anti selectivity was observed as seen in runs 6 and 7.[7]

Typical procedure is described for the synthesis of β-sulfenyl alcohol **3b**: Under a nitrogen atmosphere at –78 °C, to a stirred suspension of $Cp_2Zr(H)Cl$[8] (322 mg, 1.25 mmol) in CH_2Cl_2 (1.0 ml) [for a special precaution to prepare the suspension, see Ref. 3b] was added allenyl sulfide **1**[4] (330 mg,

Table 1. Reaction of **2** with aldehydes and ketones[a]

run	aldehyde or methyl ketone	product[b] (yield/%, anti/syn)
1	n-$C_5H_{11}CHO$	 **3a** (75, 93/7)
2		 **3b** (81, >97/3)
3		 **3c** (80, 95/5)
4		 **3d** (80, 86/14)
5	n-$C_{13}H_{27}COCH_3$	 **3e** (81, 82/18)
6		 **3f** (80, 96/4)
7		 **3g** (94, 88/12)

[a]Reaction conditions: –78 °C, 30 min for runs 1–4; 0 °C, 1 h for runs 5–7. [b]Each of the major stereoisomers is depicted.

2.23 mmol) in CH_2Cl_2 (2.5 ml). The reaction was gradually warmed up to room temperature, where a red solution resulted. The reaction was rechilled to –78 °C, to which a solution of cyclohexanecarbaldehyde (98.7 mg, 0.881 mmol) in CH_2Cl_2 (2.5 ml) was added. After 30 min, the reaction was stopped by adding sat. aqueous $NaHCO_3$. Extractive workup followed by purification (SiO_2 preparative TLC, hexane/Et_2O = 9/1) gave alcohol **3b** (186 mg, 81%).[5,6]

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References and Notes

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3 a) H. Maeta, T. Hasegawa, and K. Suzuki, *Synlett*, **1993**, 341; b) M. Chino, T. Matsumoto, and K. Suzuki, *Synlett*, **1994**, 359; c) K. Suzuki, T. Hasegawa, T. Imai, H. Maeta, and S. Ohba, *Tetrahedron*, **51**, 4483 (1995).

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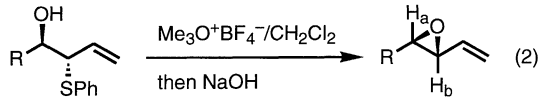
5 All new compounds were fully characterized by ^1H, ^{13}C NMR, IR, and high-resolution MS.

6 The stereoselectivities were determined by the peak integration of ^1H NMR (400 MHz). The stereochemistry was assigned by converting the major adducts **3a–c** to the corresponding vinyl epoxides **4a–c** as shown below.

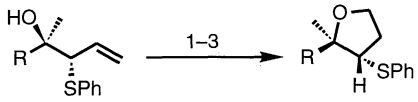


(2)

3a–c **4a–c**

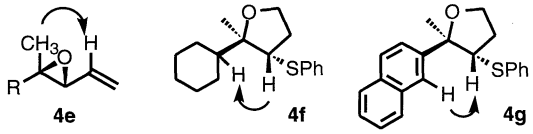
J_{a-b} = 1.8–2.0 Hz

7 The stereoselectivities were determined by the peak integration of ^1H NMR (400 MHz). The stereochemistry was assigned by the NOE experiments for vinyl epoxide **4e**, obtained from **3e** in a similar manner as in Eq. 2, and for tetrahydrofurans **4f** and **4g**, which were obtained from **3f** and **3g** (Eq. 3), respectively.



(3)

(1) 9-BBN; (2) H_2O_2, NaOH; (3) Tf_2O, 2,6-di-*tert*-butyl-4-methylpyridine.



(⟶ n.O.e)

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