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[3 + 2] Cycloaddition of Allylic Silane with *N*-Chlorosulfonyl Isocyanate

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Reaction of a substituted allylsilane with *N*-chlorosulfonyl isocyanate at 0 °C takes place in an unexpected manner to give a [3+2] cycloaddition product, a β-silyl-γ-lactam, rather than a [2+2] cycloadduct.

Allylsilanes are reagents of significant synthetic importance. They are widely used as nucleophiles toward electron-deficient double bonds in the presence of a reaction promoter, which may be either a Lewis acid[1] or a fluoride anion[2] that generates a nucleophile from the corresponding organosilicon compound.[3] We report here an unusual reactivity of an allylic silane toward *N*-chlorosulfonyl isocyanate (CSI); that is, (3-acetoxy)allylsilane **1** undergoes stereocontrolled [3+2] cycloaddition reaction to CSI under mild thermal conditions (0 °C) in the absence of any promoter (Fig. 1).

3-Acetoxy-1-methylallylsilane (**1**) was prepared by conjugate addition of lithium bis[dimethyl(phenyl)silyl]cuprate(I)

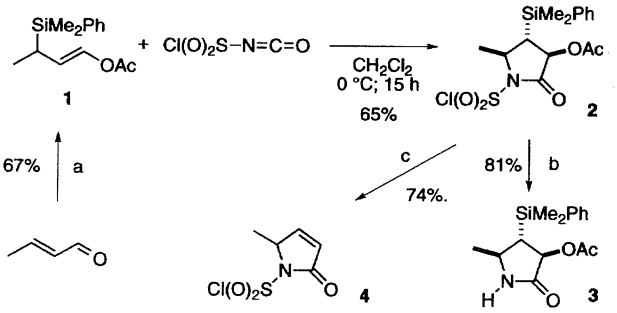

Fig. 1. [3+2] Cycloaddition of allylic silane **1** to CSI. Conditions: (a) $Li[Cu(SiMe_2Ph)_2]$, THF, −78 to −23 °C, then Ac_2O, 67%; (b) sat. Na_2SO_3, sat. $NaHCO_3$, THF, 50 °C; (c) BF_3·AcOH, CH_2Cl_2, room temperature.

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with crotonaldehyde[4] and subsequent trapping of the adduct with acetic anhydride (Fig. 1). The reaction of **1** with chlorosulfonyl isocyanate took place smoothly upon mixing them together in CH_2Cl_2 at 0 °C. Contrary to the manner expected for the reaction of CSI with simple allylsilanes,[5] the reaction gave a β-silyl-γ-lactam **2** as a single product out of the four possible stereoisomers in 65% isolated yield. The stereochemistry of the product was established by X-ray crystallographic analysis of a single crystal of **2**.

Removal of the chlorosulfonyl group on the cycloadduct to give **3** was efficiently achieved by treatment with aqueous Na_2SO_3–$NaHCO_3$ in THF at 50 °C (81%). On the other hand, treatment of **2** with BF_3·2AcOH gave an elimination product **4** in 74% yield, which conforms to the *trans*-stereochemical relationship between the silyl and acetoxy groups.

CSI has been known to undergo [2+2] cycloaddition with simple olefins,[6] vinyl acetate and electron-rich olefins[7] and unsubstituted allylsilanes to afford β-lactams.[8] The reaction is believed to proceed in a stepwise manner, and is initiated by nucleophilic attack of the olefinic part of the allylic silane to the carbonyl group of the CIS molecule. Thus, the operation of the [3+2] cycloaddition manifold in the reaction of **1** was quite unexpected, since [3+2] reaction of allylic silanes has so far been achieved only in Lewis acid mediated reactions of allylic silanes.[9]

In the light of the above general mechanism of the CSI cycloaddition and of the stereochemistry of the product, we propose that the present [3+2] cycloaddition reaction takes place through initial formation of a zwitterionic intermediate **C** as shown in Fig. 2. Through this intermediate, the 1,2-migration of the dimethyl(phenyl)silyl group takes place to give the unusual [3+2] rather than the conventional [2+2] product.

The substrate **1** has a dual character, allylsilane and vinyl acetate. The regioselectivity of **1**/CSI interaction is opposite to that observed normally for the [2+2] reaction with vinyl acetates, indicating that the electronic effect of the silyl group is much stronger than the electron-donating effects of the acetoxy group. The two ground state conformers of **1**, **A** and **B**, wherein the C–Si σ-bond and the olefin π-orbital are conjugated with each other, are possible reactive conformers leading to the product **2**. On the basis of the product stereochemistry, we can surmise that the reaction has taken place via the conformer **A**.

In summary, we found that the reaction of CSI with a substituted allylic silane provides a new example of an uncatalyzed [3+2] cycloaddition pathway of allylic silane. Taken together with the recent work by Woerpel reporting similar reactions of allylsilanes with different substituents,[5] the present results provide the prospect that the allylsilane/CSI

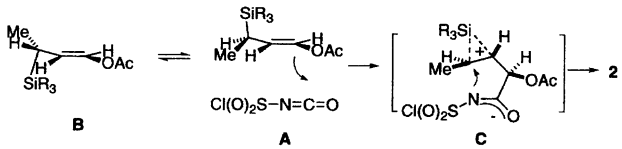

Fig. 2. Regio- and stereochemistry in the formation of **2**.

reaction will be a useful method for the synthesis of γ-lactam and γ-amino acid derivatives.[10]

Experimental[11]

(*E*)- (3- Acetoxy- 1- methylallyl)dimethyl(phenyl)silane (1). Crotonaldehyde (0.61 mL, 7.4 mmol) is added to a THF solution of Li[Cu(SiMe$_2$Ph)$_2$] (7.4 mmol) at −78 °C. After stirring for 1 h at −70 °C and 2.5 h at −23 °C, acetic anhydride (4.5 mL, 48 mmol) was added and the mixture was stirred for 12 h at room temperature. The mixture was diluted with Et_2O and washed with 1 M (1 M = 1 mol dm^{-3}) HCl, sat. $NaHCO_3$, and sat. NaCl, dried over magnesium sulfate, filtered, and finally concentrated under reduced pressure. Purification by column chromatography on silica gel gave the title compound as a colorless oil (1.24 g, 67%): IR (neat) 2950, 1755, 1370, 1370, 1220, 1110, 930, 810, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.29 (s, 3 H), 1.05 (d, J = 7.4 Hz, 3 H), 1.75 (m, 1 H), 2.11 (s, 3 H), 5.44 (dd, J = 8.4, 12.7 Hz, 1 H), 6.90 (dd, J = 1.5, 12.7 Hz, 1 H), 7.30—7.35 (m, 3 H), 7.45—7.50 (m, 2 H).

(3*R, 4*R**, 5*R**)-(±)-3-Acetoxy-1-chlorosulfonyl-4-[dimethyl(phenyl)silyl]-5-methylpyrrolidin-2-one (2).** To a solution of the allylsilane **1** (497 mg, 2.0 mmol) in 0.8 mL of CH_2Cl_2 at 0 °C was added chlorosulfonyl isocyanate (0.261 mL, 3.0 mmol) over 1 min and the mixture was stirred for 15 h. Then the mixture was diluted with CH_2Cl_2 and washed with sat. $NaHCO_3$, and the water layer was extracted with chloroform. The combined extracts were washed with sat. NaCl, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to obtain a yellow oil. Column chromatography on silica gel gave the title compound as a white solid (510 mg, 65%). Samples for elemental analysis and X-ray crystallographic analysis were prepared by recrystallization from CCl_4–hexane: Mp 97—97.5 °C; R_f = 0.25 (10% ethyl acetate in hexane); IR (CCl_4) 1780, 1755, 1420, 1220, 1180, 600 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.46 (s, 6 H), 1.54 (d, J = 6.1 Hz, 3 H), 1.57 (dd, J = 6.5, 7.8 Hz, 1 H), 4.22 (dq, J = 6.0, 6.0 Hz, 1 H), 5.38 (d, J = 7.8 Hz, 1 H), 7.35—7.60 (m, 5 H).

Anal. Calcd for $C_{15}H_{20}NO_5SiSCl$: C, 46.20; H, 5.17; N, 3.59; S, 8.22%. Found: C, 46.41; H, 5.10; N, 3.29; S, 8.20%.

(3*R, 4*R**, 5*R**)-(±)-3-Acetoxy-4-[dimethyl(phenyl)silyl)-5-methylpyrrolidin-2-one (3).** To a solution of *N*-chlorosulfonyl-γ-lactam **2** (81.8 mg, 0.21 mmol) in 0.4 mL of THF was added sat. $NaHCO_3$ (0.4 mL) and sat. Na_2SO_3 (0.4 mL), and the mixture was heated 10 min at 50 °C. The aqueous layer was extracted with ethyl acetate, and the combined extracts were washed with sat. NaCl, dried over magnesium sulfate, filtered, and concentrated. Column chromatography on silica gel (70% ethyl acetate in hexane) gave the title compound as white solid (49.6 mg, 81%). Further purification was achieved by recrystallization from ethyl acetate–hexane: Mp 115—115.5 °C; R_f = 0.20 (50% ethyl acetate in hexane); IR ($CHCl_3$) 3420, 1740, 1715, 1375, 1235, 1110 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.39 (s, 3 H), 0.40 (s, 3 H), 1.14 (d, J = 6.0 Hz, 3 H), 1.55 (dd, J = 8.2, 9.7 Hz, 1 H), 1.97 (s, 3 H), 3.55 (m, 1 H), 5.45 (d, J = 9.8 Hz, 1 H), 5.89 (br s, 1 H), 7.35—7.40 (m, 3 H), 7.45—7.50 (m, 2 H). Found: C, 61.95; H, 7.36; N, 4.98%. Calcd for $C_{15}H_{21}NO_3Si$: C, 61.82; H, 7.26; N, 4.81%.

1-Chlorosulfonyl-5-methylpyrrol-2(5*H*)-one (4). A solution of γ-lactam **2** (70 mg, 0.18 mmol) in 0.3 mL of CH_2Cl_2 was treated at room temperature with BF_3·2AcOH (116 μL, 1.16 mmol). The mixture was washed with sat. $NaHCO_3$, and the water layer was extracted with ethyl acetate. The combined extracts were washed with sat. NaCl, dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Column chromatography on silica gel (30% ethyl acetate in hexane) gave the title compound as a white solid (26.1 mg, 74%): Mp 92.5—93 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.66 (d, J = 6.9 Hz, 3 H), 4.94 (ddq, J = 1.9, 1.9, 6.9 Hz, 1 H), 7.22 (dd, J = 1.9, 6.1 Hz, 1 H), 7.38 (dd, J = 2.1, 6.3 Hz, 1 H). Found: C, 30.62; H, 2.98; N, 7.39%. Calcd for $C_5H_6NO_3SCl$: C, 30.70; H, 3.09; N, 7.16%.

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