

Allyldiisopropylphenylsilane as a synthetic equivalent of 2-hydroxy-1,3-dipole. Stereoselective synthesis of cyclopentanols

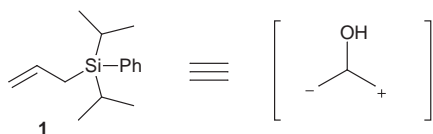
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ZrCl₄-Promoted [3 + 2] cycloaddition of allyldiisopropylphenylsilane to α,β -unsaturated ketones proceeds smoothly to afford silyl-substituted cyclopentanes highly stereoselectively. Oxidative cleavage of the carbon–silicon bond leads to stereoselective formation of cyclopentanols.

Cycloaddition reactions are one of the most widely used reactions in organic synthesis for the construction of carbocycles as well as heterocycles.¹ There is currently widespread interest² in Lewis acid-promoted [3 + 2] as well as [2 + 2] cycloaddition of allyltriisopropylsilane as a tool for constructing both 5-membered^{3,4} and 4-membered silyl-substituted ring compounds⁵ stereoselectively. We have already reported the highly stereoselective formation of silyl-substituted tetrahydrofurans by tin(IV) chloride-mediated [3 + 2] cycloaddition of allylsilane.⁶ Furthermore, titanium(IV) chloride⁷- or zirconium(IV) chloride⁸-promoted [2 + 2] cycloaddition of allyl-*tert*-butyldiphenylsilane with carbonyl compounds afforded silyl-substituted oxetanes in good yields. Use of allylsilanes bearing bulky silyl substituents, which suppress formation of the corresponding Sakurai products, is essential for the formation of the cycloadducts in high yields.

Although oxidative cleavage of the carbon–silicon bond is a well documented method for the stereoselective formation of alcohols,⁹ sterically demanding silyl groups are reported to resist the cleavage reaction.^{10,11} Hence, development of a novel allylsilane which meets the following requirements is desired: (1) cycloadducts are formed in high yields, (2) the silyl group is highly susceptible to oxidative cleavage. Along these lines, Knölker *et al.* and Meyers *et al.* have developed allyltriphenylsilane¹² and allyldimethyltritylsilane,¹³ respectively.



We focused on allyldiisopropylphenylsilane¹⁴ **1**, possessing both bulky isopropyl and phenyl moieties on the silyl group. We studied the [3 + 2] cycloaddition of the allylsilane with α,β -unsaturated ketones as probes and found that **1** falls into the above criteria as a useful 2-hydroxy-1,3-dipole; ZrCl₄-mediated [3 + 2] cycloaddition of the α,β -unsaturated ketone proceeded smoothly to afford silyl-substituted cyclopentanes highly stereoselectivity, and oxidative cleavage of the carbon–silicon bond took place smoothly to furnish cyclopentanols in high yields (see Table 1).

At the outset, titanium(IV) chloride-mediated [3 + 2] cycloaddition of **1** with methyl vinyl ketone in CH₂Cl₂ at

–78 °C furnished **2a** in 65% yield.¹⁵ Gratifyingly, use of zirconium(IV) chloride, which was effective for the formation of oxetanes,⁸ as a Lewis acid in toluene at –78 °C to –20 °C, provided **2a** in 89% yield as a single stereoisomer.¹⁶ The cycloaddition reaction with α -methylene cycloalkanones^{3g} took place smoothly in halogenated solvents to afford silyl-substituted spiro compounds (**2c–e**) in good yields (Entries 3–5). Use of 4 Å molecular sieves was not mandatory for the present cycloaddition to proceed but tended to afford the cycloadducts in reproducible yields.

Transformation of the diisopropylphenylsilyl moiety to a hydroxy group was successfully achieved in 2 steps (Table 2).¹⁷ Protodesilylation of the phenyl group with fluoride proceeded smoothly under the influence of 4.7 equiv. of HBF₄·OEt₂^{18,19} at room temperature for 26–30 h to give the corresponding fluorosilanes (**3b–e**) in excellent yields. Only when a ketone bearing an α -proton at the stereogenic center (**2a**) was employed, was the corresponding fluorosilane (**3a**) obtained as a 1 : 1 mixture of *cis*- and *trans*-isomer. Transformation of **3** to **4** was successfully achieved by slight modification of the Tamao oxidation protocol.²⁰ Buⁿ₄N·F was found to be more reactive than KF as a fluoride source. Thus, treatment of fluorides **3** with H₂O₂ (20 mol equiv.), Buⁿ₄N·F (3 equiv.) and KHCO₃ (2 equiv.) in MeOH–THF at 65 °C for 5–6 h furnished the

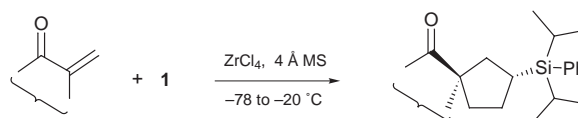


Table 1 [3 + 2] Cycloaddition of **1**

Entry	Starting material	Solvent	Product ^a	Yield (%)
1		toluene		89 ^b
2		toluene		77 ^b
3		ClCH ₂ CH ₂ Cl		74
4		ClCH ₂ CH ₂ Cl		74
5		CH ₂ Cl ₂		60

^a Compounds **2** gave satisfactory spectroscopic and analytical data.

^b The reaction was carried out without 4 Å MS.

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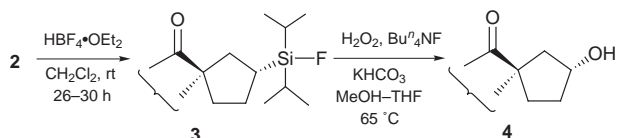


Table 2 Oxidative cleavage of the carbon–silicon bond

Entry	Starting material	Yield of fluoride (%) ^a	Yield of alcohol (%) ^a
1	2a	3a ; 82 ^b	—
2	2b	3c ; 95	4b ; 94
3	2c	3c ; 90	4c ; 87
4	2d	3d ; 99	4d ; 87
5	2e	3e ; 100	4e ; 71

^a Compounds **3** and **4** gave satisfactory spectroscopic and analytical data. ^b Obtained as 1:1 mixture of *cis*- and *trans*-isomers.

corresponding alcohols (**4b–e**) in high yields. At lower temperatures, yields of **4** dropped significantly.

In summary, allyldiisopropylphenylsilane has proven to be remarkably useful with respect to both its high reactivity toward cycloannulation and its susceptibility toward oxidative cleavage.

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 - Although Knölker reported one example of the cycloaddition of **1**, transformation of the silyl group into an OH group has not been reported.^{3b,3h}
 - Tin(IV) chloride mediated reaction gave rise to **2a** in 58% yield.
 - A typical experimental procedure for the preparation of **2a** is described (Entry 1, Table 1). To a solution of methyl vinyl ketone (25.2 mg, 0.36 mmol) in toluene (1.0 ml) was added zirconium(IV) chloride (95.2 mg, 0.41 mmol) at -20°C . After being stirred at that temperature for 10 min, the suspension was cooled to -78°C and allyldiisopropylphenylsilane (94.9 mg, 0.408 mmol) in toluene (0.8 ml) was added. The reaction mixture was allowed to warm to -20°C over 5 h and was quenched by addition of 5% aqueous KHSO_4 . The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated to dryness. Purification of the crude mixture by column chromatography (SiO_2 , hexane–ethyl acetate = 15:1, v/v) gave **2a** (102 mg, 89%).
 - It should be noted that allyl-*tert*-butyldiphenylsilane which was useful for the oxetane formation was not effective for the present cyclopentane annulation; the corresponding cycloadduct was obtained in only modest yield and oxidative cleavage of the *tert*-butyldiphenylsilyl group was not successful under the above conditions.
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