

Lewis Acid-Promoted Cycloaddition Reaction of Cyclopropanes with Allylsilanes

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The treatment of cyclopropanes having donor and acceptor substituents at the vicinal positions on the cyclopropane ring with a Lewis acid readily generates a 1,3-zwitterion, which reacted with allylsilanes to produce cycloadducts and allylic products. It was found that the yield of the cycloadduct depends on the steric demand of the alkyl substituents on the silicon atom.

Key words cyclopropane; allylsilane; zwitterion; cycloaddition

The Lewis acid-promoted allylation of allylsilanes to carbonyl compounds is a most important method for the carbon-carbon bond formation in organic synthesis.¹⁾ In addition, allylsilanes are excellent reagents for the construction of four- and five-membered ring systems because they function as the synthetic equivalent of the silyl-substituted 1,2- and/or 1,3-dipole.²⁾ Several groups have reported the synthesis of carbonyl and heterocyclic compounds by the cycloaddition reactions of allylsilanes with activated C=X π -bonds.^{3,4)} Recently, we reported a novel preparation method for the tetrahydrofurans by the reaction of allylsilanes with the α,β -epoxy alcohol derivatives.⁵⁾ On the other hand, cyclopropanes having an electron-withdrawing or donating group are susceptible to ring-opening reactions.⁶⁾ Especially, cyclopropanes with donor and acceptor substituents at the vicinal positions on the cyclopropane ring are equivalent to a ring-opened 1,3-zwitterion, which is expected to react with both nucleophiles and electrophiles.⁷⁾ Based on these facts, we demonstrated the interesting cycloaddition reaction of allylsilanes with cyclopropane derivatives (Chart 1). We now report the reaction of the allylsilane as the synthetic equivalent of the 1,2-dipole with the three-carbon 1,3-zwitterion generated from the cyclopropane.

We chose the cyclopropane (**1**)⁸⁾ as the donor-acceptor-substituted cyclopropane and examined the reaction with allylsilanes. In the presence of TiCl₄ (1.1 eq), cyclopropane (**1**) smoothly reacted with allyltrimethylsilane (allyl TMS) in CH₂Cl₂ at -78 °C to give the desired cycloadduct (**2a**) and the allylic product (**3**) in 23% (*cis*:*trans*=74:26) and 47%

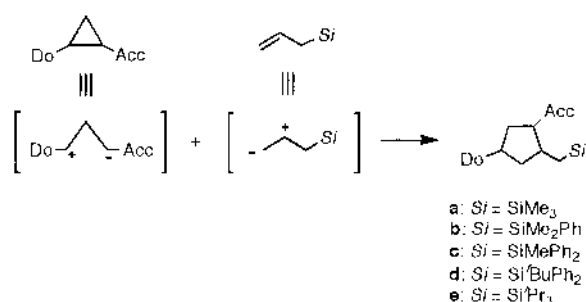


Chart 1

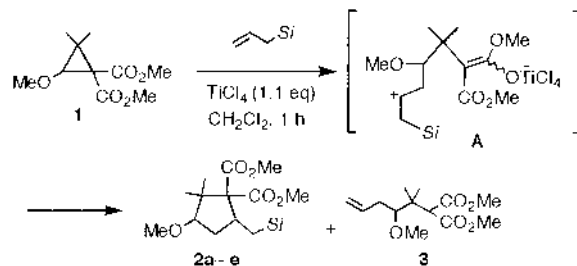
yields, respectively. Other allylsilanes were then examined and these results are summarized in Table 1. All reactions smoothly proceeded under the same reaction conditions to afford the corresponding cycloadduct and allylic product.⁹⁾ We found that the yield of the cycloadduct depends on the steric demand of the alkyl substituents on the silicon atom.^{3a-j,4c-i)} Namely, the [3+2] adduct (**2a**) was produced in only a 23% yield during the reaction of **1** with allyl TMS, while in the reaction of the sterically bulky allyltriisopropylsilane (allyl TIPS), the adduct (**2e**) was obtained in a 68% yield and no allylic product was detected (entry 5). It was also found that the stereoselectivity of the cycloadduct decreased when the reaction temperature was raised to -20 °C (entry 6). The reaction pathway for the formation of the cyclopentane derivative possibly involves the initial nucleophilic attack of the allylsilane on a zwitterion generated from **1** by the action of a Lewis acid followed by cyclization of the resulting intermediate (**A**).

To extend the scope of this methodology, we next examined the ring-expansion reaction of methanochromanone¹⁰⁾ as the condensed-ring compound. Under the Lewis acid-promoted conditions, methanochromanones (**4**, **5**) are the equivalent of a cyclic zwitterion because they have an alkoxy group as a donor and a carbonyl group as an acceptor on the benzopyran ring.¹¹⁾ The results of the reaction of methanochromanones (**4**, **5**) with allylsilanes are summarized in Table 2. All reactions smoothly proceeded in the presence of a catalytic amount of the trimethylsilyl trifluoromethanesulfonate (TMSOTf) to give the cycloadducts (**6**–**9**) and 2-allyl-1-benzoxepinone (**10**), and that typical Lewis acids such as TiCl₄ and SnCl₄ were not effective in this reaction. Similar to the simple cyclopropane (**1**), the cycloadduct was formed as the major product when the sterically bulky allyl TIPS was used (entries 2, 4).

The stereochemical assignment of the cycloadducts (*cis*-**2e**, **6e**) was mainly established by analysis of their nuclear Overhauser effect (NOE) experiments and other cycloadducts were assigned in a comparative analysis of the ¹H-NMR spectra (Fig. 1).

In summary, we have demonstrated that the Lewis acid-

Table 1. Ring-Expansion Reaction of Cyclopropane (**1**) with Allylsilanes



Entry	Si	Temp./°C	Yield 2/(%) ^{a)}	<i>cis</i> : <i>trans</i> ^{b)}	Yield 3/(%) ^{a)}
1	SiMe ₃	-78	23	74:26	47
2	SiMe ₂ Ph	-78	45	63:37	51
3	SiMePh ₂	-78	48	67:33	32
4	Si ^t BuPh ₂	-78	65	83:17	24
5	Si ⁱ Pr ₃	-78	68	91:9	0
6	Si ⁱ Pr ₃	-20	70	76:24	12

a) Isolated yield. b) The ratio of the stereoisomers was determined by ¹H-NMR.

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Table 2. Ring-Expansion Reaction of Methanochromanones (4, 5) with Allylsilanes

4: R¹=Me, R²=H
5: R¹=R²=Me

6: R¹=Me, R²=H
7: R¹=H²=Me
8: R¹=Me, R²=H
9: R¹=R²=Me

Entry	Cyclopropane	Si	Cycloadduct Yield/(%) ^{a)}	6, 7: 8, 9 ^{b)}	Yield 10 ^{c)} (%)
1	4	SiMe ₃	16	77:23	40
2	4	Si ⁱ Pr ₃	83	67:33	3
3	5	SiMe ₃	0	—	94 ^{c)}
4	5	Si ⁱ Pr ₃	80	71:29	16 ^{c)}

a) Isolated yield. b) The ratio of the stereoisomers was determined by ¹H-NMR. c) Isolated as a 1.4:1 diastereomeric mixture.

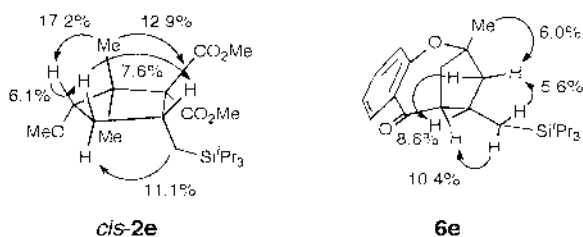


Fig. 1

promoted reactions of donor–acceptor-substituted cyclopropanes with allylsilanes smoothly proceeded to afford the corresponding cycloadducts in good yields. The mechanistic aspects and further applications of this reaction are now under investigation in our laboratory.

References and notes

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