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Acid-catalyzed reaction behavior of 1-silylcyclopropylmethanols

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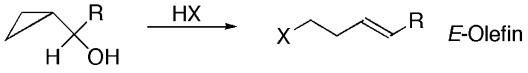
Abstract—Treatment of 1-silylcyclopropylmethanols with TsOH in methanol gives different homoallyl ethers depending upon the configuration of substituents on cyclopropane ring and the kinds of substituents on carbinyl carbon. Especially, the reaction of cyclopropylmethanols having no substituents on the same side with silyl group on cyclopropane ring proceeds to give the corresponding *E*-homoallyl ethers with high stereoselectivity. The following protiodesilylation of resulting homoallyl ethers proceeds with retention of configuration.

Cyclopropylcarbinyl cations are interesting species[1] and have been used extensively as useful intermediates in organic synthesis.[2] Especially, homoallylic rearrangement of cyclopropylcarbinyl cation is known as the Julia olefin synthesis that leads to stereoselective formation of the *E*-homoallyl derivatives (Scheme 1).[3–5] In contrast, we have recently reported that the homoallylic rearrangement of cyclopropylsilylcarbinyl cation having a *n*-, *s*-alkyl group on carbinyl carbon led to stereoselective formation of *E*-silyl-substituted homoallyl derivatives[6] and the following protiodesilylation proceeded with retention of configuration (Scheme 2).[5a] In consequence, we presented that a bulky silyl group acted as a directing group for the stereoselectivity on this olefin synthesis and the geometry of the alkene moiety of protiodesilylated products was the opposite to that of Julia reaction using the corresponding cyclopropylmethanols. However, the reaction of cyclopropylsilylcarbinyl cation having a bulky alkyl group such as a *t*-butyl



Scheme 1. Julia olefin synthesis.

Keywords: Cyclopropylmethanol; Homoallylic rearrangement; Trimethylsilyl group; Protiodesilylation.
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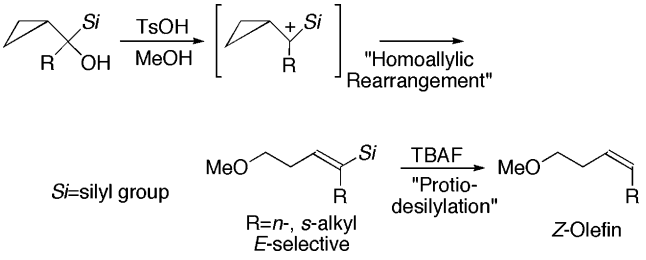
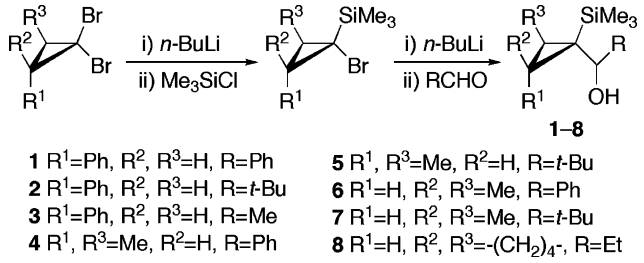


Scheme 2. Stereoselective construction of *Z*-homoallyl derivatives from cyclopropylsilylmethanols.

group on carbinyl carbon gave the undesired *Z*-isomer exclusively. The above observation led to us to attempt the homoallylic rearrangement of cyclopropylcarbinyl cation having a silyl group at the 1-position of cyclopropane ring,[7] which may afford *E*-silyl-substituted homoallyl derivatives effectively. In this letter, we describe the generation of cyclopropylcarbinyl cations by the reaction of 1-silylcyclopropylmethanols with acid-catalyst and then following the rearrangement reaction behavior. Furthermore, the protiodesilylation[8] of the resulting silyl-substituted homoallylic compounds for stereoselective formation of *Z*-homoallyl derivatives is reported.

The preparation of 1-silylcyclopropylmethanols **1**–**8** was accomplished as follows (Scheme 3). The treatment of



Scheme 3. Preparation of 1-trimethylsilylcyclopropylmethanols.

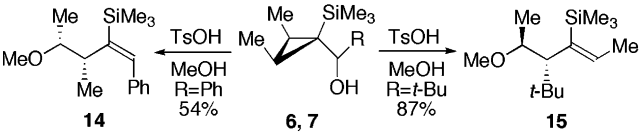
dibromocyclopropanes with *n*-butyllithium followed by reaction with chlorotrimethylsilane gave the corresponding trimethylsilylcyclopropane derivatives in high yields.[9] The resulting cyclopropane derivatives were treated with *n*-butyllithium and the subsequent reaction with aldehyde gave the desired cyclopropylmethanols **1**–**8**. Incidentally, the bicyclic compound **8** was yielded as a mixture of cis and trans isomers. Therefore, this mixture was separated by column chromatography on silica-gel, and then each isomer was used as a starting material.

The silylcyclopropylmethanols **1**–**3** having a phenyl group that is located on the opposite site of silyl group on cyclopropane ring were treated with TsOH in methanol. The homoallylic rearrangement proceeded to give the *Z*-isomer of silyl-substituted homoallyl ethers **9**–**11** in moderate to high yields, with high stereoselectivity independent of the kind of the substituent on carbinyl carbon (Scheme 4).[10,11] In this reaction, the cleavage of C1–C2 bond of the cyclopropane ring was observed exclusively. Similarly, the reaction of 2,3-*trans*-dimethylcyclopropylmethanols **4** and **5** was smoothly proceeded to afford the corresponding 1,2-*anti*-3*Z*-homoallyl ethers **12** and **13** (Scheme 5). It should be noted that the epimerization was not observed in this rearrangement reaction.

More noteworthy, the same reaction of 2,3-cis isomer **6** having a phenyl group on the carbinyl carbon afforded the 1,2-*syn*-3*E*-isomer **14** selectively (Scheme 6). However, the reaction of **7** having a *t*-butyl group on the carbinyl carbon provided 1,2-*anti*-3*Z*-homoallyl ether derivative **15** having the *t*-butyl group at allylic position.

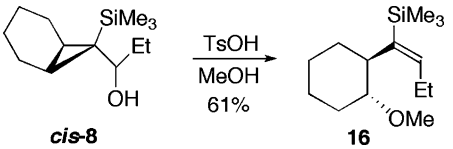
In the reaction of bicyclic compound **8**, cis isomer reacted to give the corresponding *anti*-*E*-isomer **16** as with the reaction of **6** (Scheme 7). On the other hand, the reaction of *trans*-**8** proceeded to afford *Z*-homoallyl ether **17** (Scheme 8).

These results suggest that the stereochemistry of homoallylic rearrangement of the silylcyclopropylmethanols is dependent on the configuration of substituents on the three-membered ring. Thus, the following mechanism for the reaction was proposed (Schemes 9 and 10). For the reaction of cyclopropylmethanols having a substituent (Ph or Me) located on the opposite site of silyl group on cyclopropane ring, the acid protonates at the oxygen atom of starting alcohols and bisected cation species[3a,5,12] **A** and **B** are formed (Scheme 9). The formation of bisected cation **A** seems to be favored compared to **B** by the less strain between R group and R^1 group on the three-membered ring. Thus, *Z*-silylalkenes **9**–**13** are formed selectively. Since the attack of methanol to cation intermediate **A** proceeds in an S_N2' manner, no epimerization is observed at all. On the other hand, in the case of the reaction using 2,3-*cis*-dimethylcyclopropylmethanols, bisected cation **C** is formed exclusively (Scheme 10). As a result, the reaction leads to 1,2-*syn*-3*E*-silylalkene **14** with high stereoselectivity. In contrast, to avoid the formation of steric hindered trisubstituted alkene, the cation **C** would be transformed to a more stable cation species **D** via bicyclobutonium ions[1a,13] in the reaction of 2,3-*cis*-dimethylcyclopropylmethanols having a *t*-butyl group on the carbinyl carbon. Conse-

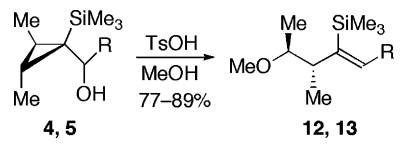


Scheme 6. Homoallylic rearrangement of 1-silyl substituted 2,3-*cis*-dimethylcyclopropylmethanols.

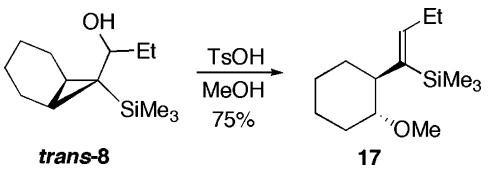
Scheme 4. Homoallylic rearrangement of 2-phenyl-1-silylcyclopropylmethanols.



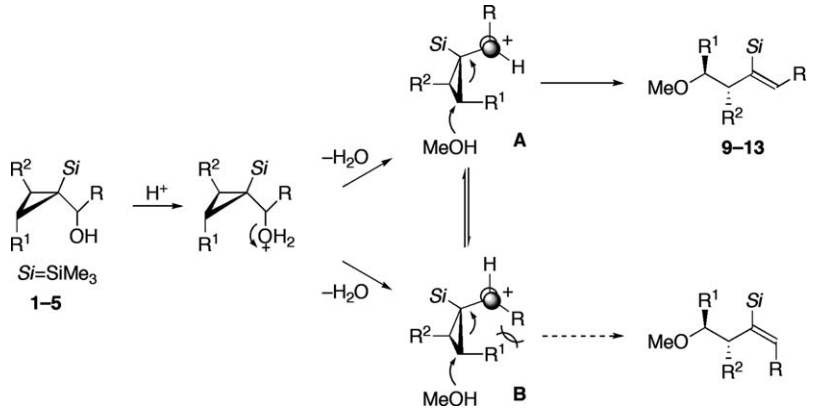
Scheme 7. Homoallylic rearrangement of 7-silyl substituted *cis*-bicyclo[4.1.0]hept-7-ylmethanol **8**.



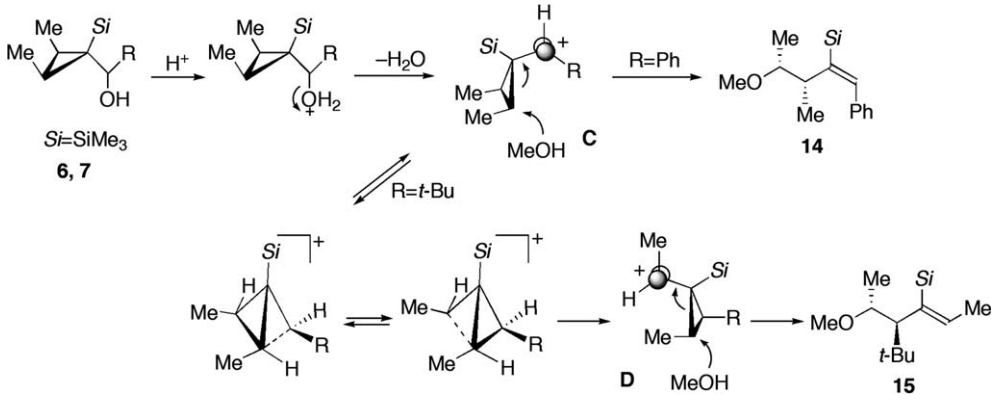
Scheme 5. Homoallylic rearrangement of 1-silyl substituted 2,3-*trans*-dimethylcyclopropylmethanols.



Scheme 8. Homoallylic rearrangement of 7-silyl substituted *trans*-bicyclo[4.1.0]hept-7-ylmethanol **8**.



Scheme 9. Mechanism of the homoallylic rearrangements of silylcyclopropylmethanols **1**–**5**.

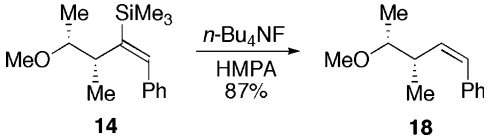


Scheme 10. Mechanism of the homoallylic rearrangements of 2,3-*cis*-dimethylcyclopropylmethanols.

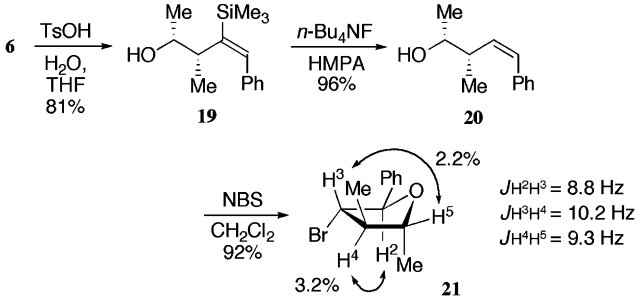
quently, 1,2-*anti*-3*Z*-silylalkene **15** was yielded with high stereoselectivity. The reaction of bicyclic compounds **8** would proceed similarly as mentioned above.

The protiodesilylation of vinylsilane proceeds with complete retention of the configuration.[8] Thus, protiodesilylation of resulting *E*-silyl-substituted homoallyl derivative **14** was examined and the result is shown in Scheme 11. Treatment of **14** with tetrabutylammonium fluoride (TBAF) in hexamethylphosphoric triamide gave the corresponding *Z*-protiodesilylated compound **18**. Thus, it was found that the geometry of the alkene moiety of protiodesilylated products is the opposite to that of Julia reaction using the corresponding cyclopropylmethanols.

Stereochemical assignment of homoallyl derivatives was performed as follows (Scheme 12). The reaction of silylcyclopropylmethanol **6** with TsOH in water/THF proceeded to give the corresponding homoallyl alcohol **19**



Scheme 11. Protiodesilylation of homoallyl ether **14**.



Scheme 12. Conversion of **6** into tetrahydrofuran derivative **21**.

as with the reaction in methanol mentioned above. Treatment of the resulting alcohol **19** with TBAF followed by intramolecular bromo etherification with NBS gave the corresponding tetrahydrofuran derivative **21**.[14] The vicinal coupling constant observed between the protons on C-4 and C-5 in the ^{1}H NMR spectrum and the NOE experiments clearly indicated the trans arrangement of two methyl groups, which is correlated to 1,2-*syn*-configuration in homoallyl alcohol **19**. Thus, the stereoconfiguration of other products was predicted by comparing with the chemical shifts and coupling constants.

In conclusion, acid-catalyzed homoallylic rearrangement of 1-silylcyclopropylmethanols has been described.

1-Silylcyclopropylmethanols reacted with TsOH in methanol to afford different homoallyl ethers depending upon the configuration of substituents on cyclopropane ring and the kinds of substituents on carbinyl carbon. Especially, the reaction of cyclopropylmethanols having no substituents on the same side with silyl group on cyclopropane ring proceeded to give the corresponding *E*-homoallyl ethers. The protiodesilylation of resulting homoallyl ethers proceeded with retention of configuration, thus it was found that the geometry of the alkene moiety of protiodesilylated products is the opposite to that of Julia reaction using the corresponding cyclopropylmethanols. Further studies are aimed at expanding the scope of these reactions, and introduction of other functional group instead of silyl group and the following the homoallylic rearrangement reaction is now in progress in our laboratory. The results will be reported in due course.

Acknowledgments

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10. Typical procedure for the homoallylic rearrangement of 1-silylcyclopropylmethanol with TsOH:1-silylcyclopropylmethanol solution (2 mmol in 10 ml of methanol) was placed in a round-bottomed flask under argon, followed by the addition of TsOH (2.4 mmol) at 0 °C. The mixture was stirred for 2 h. The reaction was quenched with a sodium hydrogen carbonate aqueous solution. The product was extracted with pentane, washed with brine, dried with anhydrous Na_2SO_4, concentrated under reduced pressure, and separated with silica gel chromatography using a mixture of hexane and dichloromethane as the eluent, affording the corresponding homoallyl ethers. Selected spectral properties of compound **14** are as follows. IR (neat): 3060, 3025, 2950, 2940, 1615, 1455, 1250, 1105, 835 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.16 (m, 5H), 6.87 (s, 1H), 3.31 (dq, 1H, $J = 8.1$, 6.1 Hz), 3.23 (s, 3H), 3.03 (dq, 1H, $J = 8.1$, 7.5 Hz), 1.06 (d, 3H, $J = 6.1$ Hz), 1.00 (d, 3H, $J = 7.5$ Hz), 0.22 (s, 9H). HRMS calcd for $C_{16}H_{26}OSi$ (M^+) 262.1753, found 262.1757.
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