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Fluoride anion-induced intramolecular cyclopropanation of allylsilanes

Airat M. Gimazetdinov *, Aidar Z. Al'mukhametov, Leonid V. Spirikhin, Mansur S. Miftakhov

Ufa Institute of Chemistry of the Russian Academy of Sciences, Prospect Oktyabrya 71, 450054 Ufa, Russian Federation

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ABSTRACT

The reaction of cyclopentenylsilane derivatives with *n*-Bu_4NF in THF at rt was shown to proceed with the regio- and stereoselective formation of the corresponding bicyclo[3.1.0]hex-2-ene derivatives.

Allylsilanes **1**–**5**, which are readily available from 5-trimethylsilyl or 5-(dimethylphenyl)silyl cyclopentadienes, have been used in the synthesis of various cyclopentitols, carbasugars, prostanoids, carbanucleosides and other compounds (Fig. 1).[1–5] It is noteworthy that in contrast to their parent non-silyl analogues, the presence of SiR_3-groups in structures **1**–**5** opens new possibilities for their application in target directed synthesis due to the non-typical chemical properties of allylsilanes,[1,6,7] e.g. the use of SiR_3 as a hydroxyl group equivalent,[6] and Brook's rearrangement with tandem transformations.[8]

In this work, we planned to implement a route for the synthesis of regioisomeric bicycles **7a** and **7b** from the previously obtained chiral lactone **5**.[5] The target compounds **7a** and **7b** represent novel functionalized chiral building blocks for use in the development of synthetic approaches towards the bioactive cyclopentanoid carbacycline and its analogues. Allylsilanes **6** were considered as intermediate compounds, which after deprotection, oxidation and an intramolecular Morita-Baylis-Hillman reaction should lead to the target bicycles **7** (Scheme 1).

The synthesis of the proposed building blocks is shown in Scheme 2. Initially, reduction of lactone **5** upon treatment with $LiAlH_4$ gave compound **8**. Monosilylation of **8** with TBDMSCl led to a 1:1 mixture of monoprotected diols **9a,b** which were sepa-

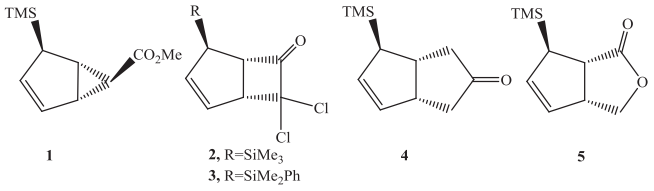
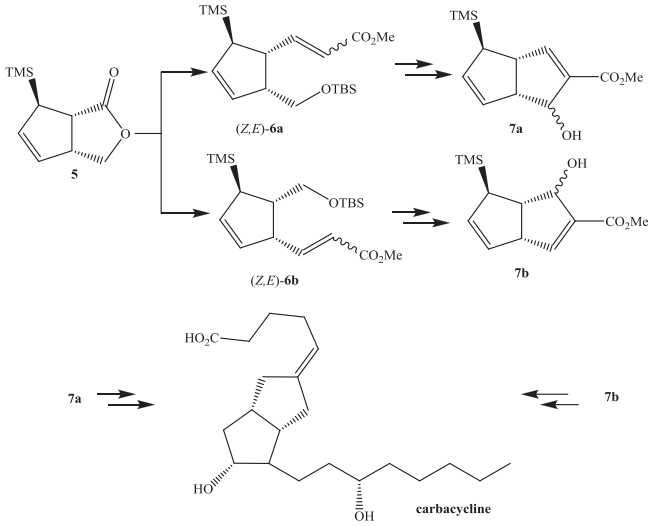


Fig. 1. Structures of allylsilanes **1**–**5**.



Scheme 1. Proposed strategy for the construction of building blocks **7a,b** for the synthesis of carbacycline.

* Corresponding author.
E-mail address: gimazetdinov@anrb.ru (A.M. Gimazetdinov).

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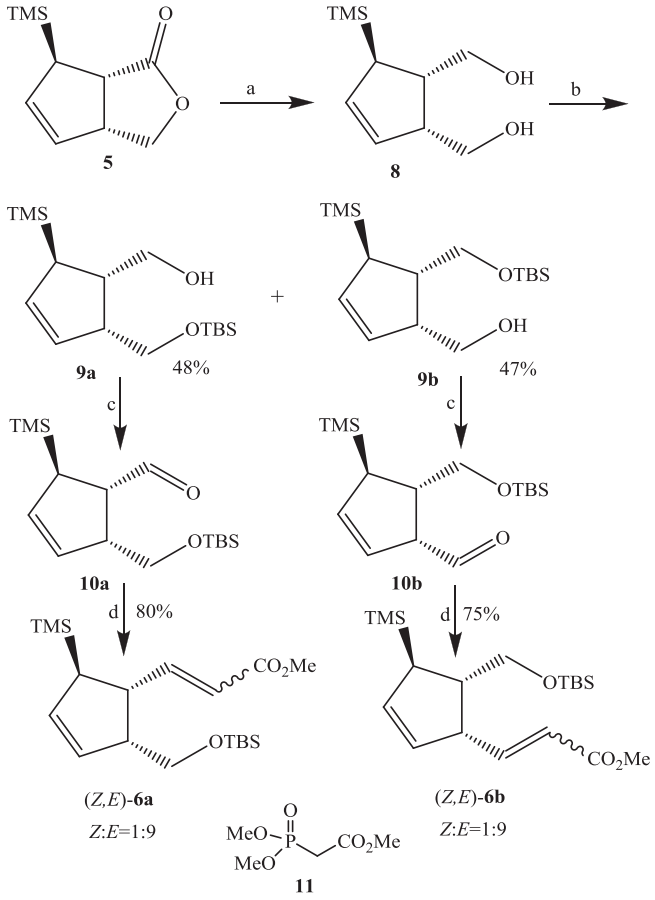
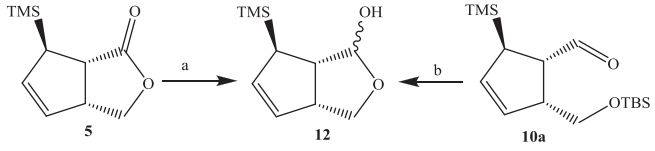
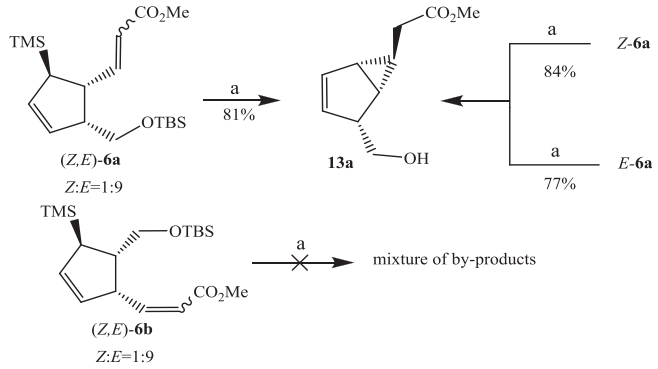


Scheme 2. Synthesis of allylsilanes **6a** and **6b**. Reagents and conditions: (a) $LiAlH_4$ (3 equiv.), THF, 0 °C, 30 min, 91%; (b) TBDMSCl (1.1 equiv.), imidazole (1.1 equiv.), CH_2Cl_2, 0 °C to rt, 8 h, 95%; (c) Oxalyl chloride (2 equiv.), DMSO (2.5 equiv.), Et_3N (5 equiv.), CH_2Cl_2, −70 °C, 1 h; (d) **11** (1.5 equiv.), NaH (1.3 equiv.), THF, 0 °C, 1 h, 75–80% (over 2 steps).



Scheme 3. Counter synthesis of lactol **12**. Reagents and conditions: (a) DIBAL-H (2.5 equiv.), CH_2Cl_2, −70 °C, 20 min, 98%; (b) Dowex (excess), CH_3OH, rt, 3 h, 89%.



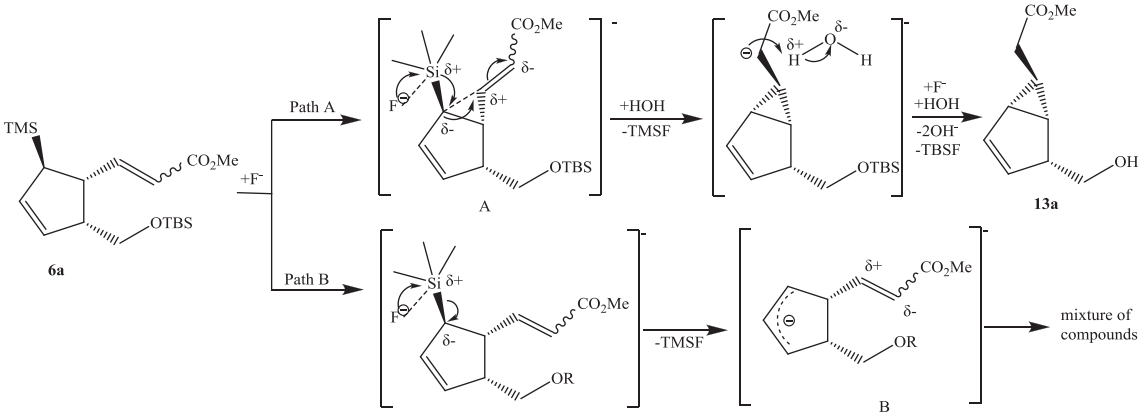
Scheme 4. Reactions of allylsilanes **6a** and **6b** with TBAF. Reagents and conditions: (a) *n*-Bu_4NF (2.0 equiv.), THF, rt, 3 h.

rated using silica gel column chromatography. The Swern oxidation of alcohols **9a,b** proceeded smoothly with formation of the corresponding regioisomeric compounds **10a,b**. The Horner-Wittig reaction of phosphonate **11** with aldehydes **10a** and **10b** was carried out without purification due to their instability during column chromatography, affording the corresponding methyl esters **6a,b** in high yield as a mixture of isomers (*Z*:*E* = 1:9). These isomers could be easily separated by silica gel column chromatography.

The structures of **9a**,**9b** and their derivatives were proven by the counter synthesis method. Thus, the DIBAL-H reduction of lactone **5** and acidic hydrolysis of **10a** using an ion exchange resin led to the same lactol **12** (Scheme 3).

The next step in our proposed strategy was cleavage of the TBS protecting group in compounds **6a,b**. However, carrying out this reaction under typical conditions using *n*-Bu_4NF led to unexpected results. The *Z,E*-mixture of allylsilane **6a** led to **13a** as the sole product in 81% yield (Scheme 4). Reaction of the individual compounds *Z*-**6a** and *E*-**6a** also led to bicycle **13a**. In contrast to **6a**, treatment of the regioisomeric allylsilane **6b** with *n*-Bu_4NF gave a mixture of by-products.

The generation of allylic anions from allylsilanes and their reaction with aldehydes was first described by Sakurai and co-workers.[9] Subsequently, intramolecular variants of this reaction were developed that allowed access to mono- and polycyclic compounds.[10] Typically, these transformations proceed under heating, however, examples of activation (*bis*-allylsilanes,[11] "push-pool"[12]) at room temperature have been reported. In the transformation **6a**→**13a**, the realization of a "push-pull" mechanismis possible. The presence of an acrylate group in a suitable position for cyclization should promote nucleophilic attack (Pathway A, Scheme 5).



Scheme 5. Possible pathways for the transformation of compound **6a**.