Tetrahedron Letters 58 (2017) 3406-3409

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Iodine-mediated rearrangements of diallylsilanes

ABSTRACT

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ARTICLE INFO

Article history: Received 6 June 2017 Revised 5 July 2017 Accepted 10 July 2017 Available online 11 July 2017

Keywords: Silacyclobutane Diallylsilane Rearrangement Cross-metathesis Amine annulation

During the course of ongoing investigations into activatable silanes for nucleophilic additions to carbonyls,¹ we became interested in exploring reactions of allylsilacyclobutane **1** (Scheme 1).² This compound has been reported to perform non-catalyzed and diastereoselective additions to α -hydroxyketones.² proceeding first through alkoxy ligand exchange followed by carbonyl activation by the Lewis acidic silacyclobutane³ and intramolecular allylation. In that original report,² compound **1** was prepared in 30% yield by adding an allyl Grignard reagent (1 equiv.) to 1,1dichlorosilacyclobutane followed by etherification with cyclohexanol (CyOH) in the presence of triethylamine (Et₃N). When attempting this chemistry, we routinely obtained very low yields of **1** rather than the expected statistical mixture. Switching the order of addition (i.e. CyOH/Et₃N followed by allylmagnesium bromide) gave similar results. Others have commented on the challenges of mono-substitution reactions of dichlorosilanes with Grignard reagents as a rationale for the development of more selective methods.^{4,5}

As part of these efforts to synthesize **1**, significant quantities of diallylsilacyclobutane **2** were recovered (*Ref.* Scheme 1). In an attempt to convert compound **2** to **1**, we turned to the iodine-promoted etherification procedure of Hosomi and Sakurai.⁶ In the event, treatment of **2** with catalytic iodine (10 mol%) in the presence of CyOH (1 equiv.) at 50 °C gave a mixture of **1**, **2**, and the diether **3** from which **1** could be consistently isolated in ca. 30% yield (Scheme 2). Currently this is our method of choice

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Diallylsilanes can be made to rearrange upon treatment with I₂. Of the silanes tested, diallyldiphenylsilane showed the greatest propensity to undergo this intramolecular carbocation allylation process. After etherification of the initially formed iodosilane, the products from this transformation represent useful synthetic intermediates, suitable for alkylation and cross-metathesis/annulation reactions.

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(reference #2)

ÒСу

3



(30%)

l₂ (10 mol%

CvOH (1 equiv)

CH2Cl2, 50 °C

(i.e. purposely synthesizing **2** followed by iodoetherification) for obtaining useful quantities of **1**.

Careful analysis of the ¹H NMR spectrum from the reaction of **2** with catalytic iodine and cyclohexanol revealed small amounts of a side product containing what appeared to be a diastereotopic methylene group (Fig. 1). Drawn suggestively, one can envision







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Fig. 1. ¹H NMR analysis of iodine-catalyzed etherification of 2 showing small amounts of putative compound 4.



Scheme 3. Previously reported electrophilic rearrangements of diallylsilanes.

how a compound of this type (**4**) might arise from an intramolecular allylation of the initially formed intermediate cation **5**.

A few other reports of related electrophile-promoted rearrangements of diallylsilanes can be found.^{7.8} For instance, Akiyama et al. reported a domino allylation of diallylsilanes to α , β -unsaturated ketones using BF₃·Et₂O (Scheme 3).⁷ For their reaction, the use of diisopropyldiallylsilane proved optimal, affording fluorosilanes of type **6** in yields between 32 and 63%. The group of Shainyan has reported a Brønsted-acid promoted rearrangement of diallylsilanes.⁸ For instance, treatment of diallyldiphenylsilane with BF₃-·2AcOH gave fluorosilane **7** in 63% yield.

Despite a rich history of allylsilane research describing both inter- and intramolecular reactions with electrophiles,⁹ the electrophile-promoted unique chemistry available to diallylsilanes remains relatively underdeveloped. Combined with the potential synthetic utility of products of type **4**, we were inspired to further investigate this apparent iodine-mediated rearrangement. It was surmised that increasing the amount of iodine should favor the process. Indeed, treatment of **2** with 1.0 equivalent of I₂ followed by treating with CyOH/Et₃N¹⁰ allowed for the isolation of ether **8** in 54% yield (Scheme 4).



Scheme 4. Iodine-mediated rearrangement of diallylsilane 2.

Substituents on silicon can have a major influence on reaction outcome.1b,11 We therefore set out to examine the impact of substitution at silicon on the selectivity of this iodination/rearrangement. As shown in Fig. 2, this was conveniently accomplished by performing the reactions in dry CDCl₃ allowing for direct monitoring of the course of the reaction by NMR. From these studies, we uncovered that diallyldiphenylsilane gave the highest ratio of rearranged compound **9** to non-rearranged products (7.86:1, with the formation of non-rearranged products indicated by the presence of allyl iodide). The reaction with diallyldimethylsilane gave the lowest extent of rearrangement, presumably as a result of decreased steric bulk of the silvl group. Comparing results for diallyldiphenyl- to diallyldiisopropyl silanes, however, suggests that there is also an electronic component to the selectivity for these compounds to rearrange (7.86:1 vs. 6.63:1 respectively) which may involve the ability of neighboring Si-C bonds to stabilize the initially formed cation upon alkene iodination through hyperconjugation effects (*Ref.* Scheme 3).¹²

Reactions at 60 °C and room temperature gave identical ratios of rearrangement to non-rearrangement, however cooling the reaction to 0 °C resulted in an erosion in selectivity for the rearranged product. The reaction proved favorable in chloroform (or dichloromethane), with toluene, tetrahydrofuran, DMF and DMSO all giving at best trace amounts of the corresponding rearranged product. Using our optimal conditions (diallyldiphenylsilane, 1 equiv. I₂, DCM, room temp.), ether **10** was isolated in 72% yield (Scheme 5).

We argue that the versatility of the products provided by our iodine-mediated transformation makes this a useful compliment those previously reported related methods (*Ref.* Scheme 3).^{7,8} For instance, iodide **10** could be alkylated with dimethylmalonate providing silyl diester **11** in 76% yield (Scheme 6).¹³ Cross-metathesis of **10** with methyl acrylate using the 2nd generation Grubbs' catalyst (**Ru-II**) gave **12** in very high yield.¹⁴ Compound **12** was then taken on to the silylmethyl-functionalized pyrrolidine **13** upon treatment with benzylamine which was isolated in 64% yield (85% based on recovered starting material).¹⁵ Overall, this 3-step conversion of diallyldiphenylsilane to pyrrolidine **13** represents an efficient increase in molecular complexity, producing a privileged structure¹⁶ containing yet additional reactive sites.

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