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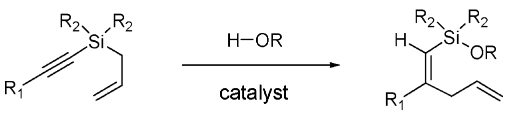
Gold-Catalyzed Intramolecular Allylation of Silyl Alkynes Induced by Silane Alcoholysis

Sangho Park and Daesung Lee*

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received April 12, 2006; E-mail: dlee@chem.wisc.edu

The pursuit of synthetic efficiency has promoted constant development of new concepts and innovated synthetic arsenals.[1] One of the most effective ways of achieving synthetic efficiency is to implement tandem reactions[2] into a synthetic sequence whereby many bond-forming and -cleaving events can occur in one synthetic operation. Following from our interest in silyl ether-based metathesis chemistry,[3] we envisioned a tandem reaction to form C−H, C−C, and Si−O bonds in one step to generate alkenyl and alkynyl silyl ethers of stereochemically defined vinyl silanes (eq 1).[4] Overall, this is a net addition of H−OR to the alkynyl allyl silanes accompanied by an allyl transfer from silicon to carbon.[5] To achieve this tandem bond formation efficiently, we propose to use carbophilic metal catalysts instead of strong mineral acid catalysts to promote the allyl transfer and the addition of H−OR to carbon and silicon centers. Herein we report a stereoselective intramolecular allylation of silyl alkynes to generate alkoxy vinyl silanes via a gold-catalyzed alcoholysis of alkynyl allyl silanes.[6]



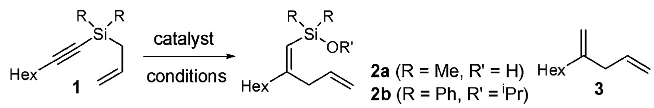
(1)

The general reactivity feature of allyl alkynyl silanes was examined with 1-octynyl allyl dimethylsilane **1a** by using several metal catalysts under different conditions (Table 1). The reaction of **1a** with $Ph_3PAuCl/AgSbF_6$ in dry CH_2Cl_2 at room temperature provided a trace amount of **2a** and **3** (entry 1).[7] However, under otherwise identical conditions in undistilled CH_2Cl_2, desilylated product **3** was obtained in 93% yield with small amount of **2a** (entry 2). Reaction with $Ph_3PAuCl/AgOTf$ gave no conversion (entry 3), whereas $PtCl_2$ (toluene, 90 °C) gave products **2a** and **3** in 20% yield (entry 5).[9] The extent of desilylation was reduced by replacing the dimethyl silyl with a diphenyl silyl group in **1b**, which, however, was recovered unchanged (entry 6) under the conditions ($Ph_3PAuCl/AgSbF_6$ in undistilled CH_2Cl_2) where **1a** gave high conversion. On the other hand, the same reaction with added ^{i}PrOH (1 equiv) provided silyl ether **2b** in good yield (75%) (entry 7). This clearly indicates that the nucleophilic assistance is crucial for an efficient transfer of an allyl group.

Having established optimized conditions for an intramolecular allyl transfer assisted by oxygen-based nucleophiles, we next examined the scope of this reaction by employing allyl silane **1c** and a variety of alcohols (Table 2). Treatment of **1c** with $Ph_3PAuCl/AgSbF_6$ in dry CH_2Cl_2 with 1°, 2°, and 3° alcohols gave good yield of products **4a−i** as inseparable mixtures of *Z*/*E*-isomers in the range of 1:1.7 to 10:1 ratio. A salient feature of these reactions is that the alkene and alkyne functionalities in the alcohol counterpart do not interfere with the reaction.

To broaden the substrate scope, substituents on the alkyne and allyl moieties were introduced (Table 3).[8] Reaction of **1b** with 4-penten-2-ol under the optimized conditions gave **5** in 71% yield with a 10:1 *Z*/*E* ratio (entry 1). Substrate **1d** with a terminal alkyne

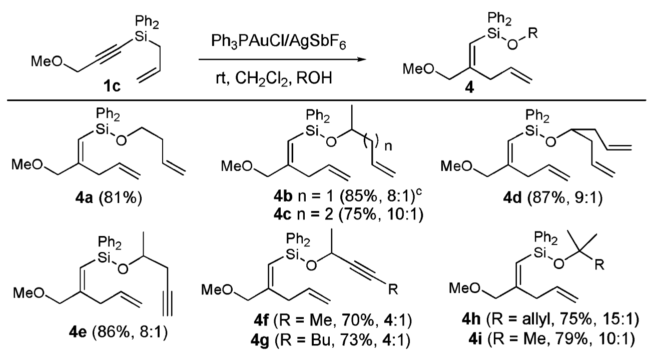
Table 1. Optimization of Catalyst and Reaction Conditions[a]



entry	enyne	R	catalyst/conditions	yield (2+3, %)	2:3[c]
1	1a	Me	$Ph_3PAuCl/AgSbF_6$, rt, dry CH_2Cl_2	traces	2:1
2			$Ph_3PAuCl/AgSbF_6$, rt, wet CH_2Cl_2[d]	93[b]	1:20
3			$Ph_3PAuCl/AgOTf$ rt, wet CH_2Cl_2[d]	traces	
4			$AuCl_3$ rt, wet CH_2Cl_2[d]	traces	
5			$PtCl_2$ 90 °C, toluene	20	2:1
6	1b	Ph	$Ph_3PAuCl/AgSbF_6$, rt, wet CH_2Cl_2[d]	traces	
7			**$Ph_3PAuCl/AgSbF_6$, rt, CH_2Cl_2 + ^{i}PrOH**	75[b]	9:1

[a] Reactions with 1 mol % of catalyst for 5−10 h. [b] Isolated yields. [c] The ratios were determined by ^{1}H NMR. [d] Undistilled CH_2Cl_2.

Table 2. Intramolecular Allylation−Alcoholysis Catalyzed by Gold[a,b]



[a] Reactions with 1 mol % of catalyst for 10 min. [b] Isolated yields are in parentheses. [c] The ratios of major:minor were determined by ^{1}H NMR.

provided **6** in 85% yield; however, the stereochemistry of the double bond was scrambled, giving 1:1.7 mixture of *Z*/*E*-isomers (entry 2). This is, probably, the consequence of isomerization of the initially formed *Z*-isomer catalyzed by either the gold catalyst or a proton.[10] Substrates **1e−g** with a methyl, phenyl, and benzyloxymethyl substituent on the alkyne behave uneventfully, giving **7−10** in good yields and *Z*/*E*-selectivity (entries 3−6). On the other hand, substrate **1h** generated more **12** than the expected product **11** (81%, **12**:**11** = 3:1). Presumably, this is the consequence of more favorable activation of the allyl group by the gold catalyst due to the presence of a sterically hindered *tert*-butyl group on the alkyne. Substrates with an alkyl substituent on the allyl segment showed variable reactivity depending on the position of the substituent compared to that of the parent system.[11] Thus, **1i** bearing a crotyl group gave excellent yields and *Z*/*E*-selectivity of **13** and **14** (entries 8 and 9), whereas the reaction of methallyl-bearing substrate **1j** provided a 1:5.5 mixture of **15** and the methallyl-displaced product **16** in 89% overall yield (entry 10).

From a mechanistic standpoint, we surmised that the activation of the alkynyl moiety of **1** by a carbophilic catalyst would induce

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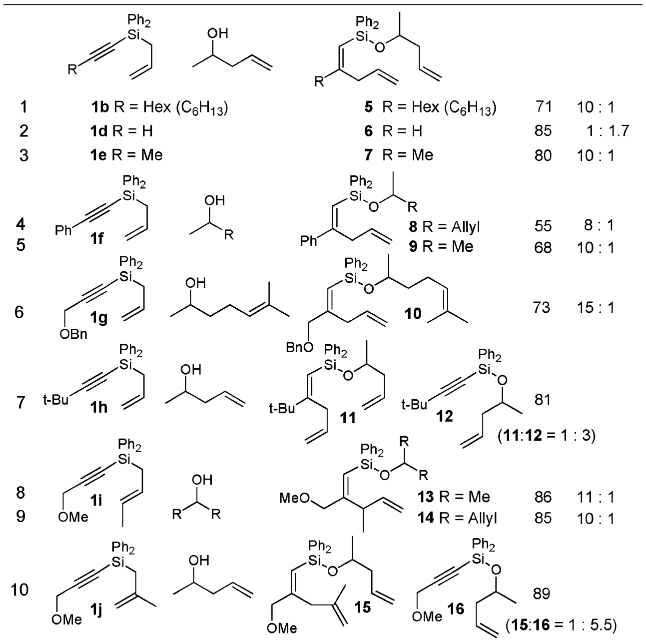
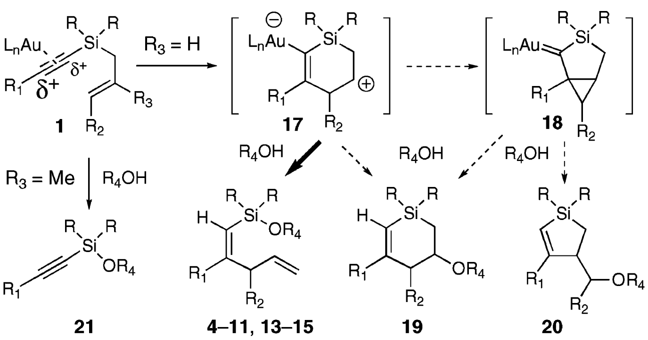
Table 3. Intramolecular Allylation−Alcoholysis Catalyzed by Gold[a]



entry	enyne	alcohol	product	yield(%)[b]	Z:E[c,d]
1	**1b** R = Hex (C_6H_{13})		**5** R = Hex (C_6H_{13})	71	10 : 1
2	**1d** R = H		**6** R = H	85	1 : 1.7
3	**1e** R = Me		**7** R = Me	80	10 : 1
4	**1f**		**8** R = Allyl	55	8 : 1
5	**1f**		**9** R = Me	68	10 : 1
6	**1g**		**10**	73	15 : 1
7	**1h**		**11**, **12**	81 (**11**:**12** = 1 : 3)	
8	**1i**		**13** R = Me	86	11 : 1
9	**1i**		**14** R = Allyl	85	10 : 1
10	**1j**		**15**, **16**	89 (**15**:**16** = 1 : 5.5)	

[a] Reactions with 1 mol % of catalyst for 10 min. [b] Isolated yields. [c] The *Z*/*E* ratios were determined by ^{1}H NMR. [d] The initially formed isomers with the silyl and allyl groups in *cis*-orientation are defined as the *Z*-isomer.

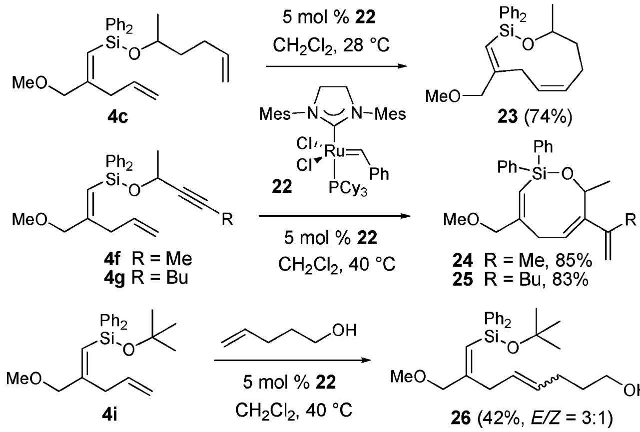
Scheme 1. Gold-Catalyzed Reorganization of Alkynyl Allyl Silane



6-endo mode attack[12] over that of 5-exo by the pendant allyl silyl moiety to generate intermediate **17** due to the *β*-silyl effect on the alkyne moiety (Scheme 1). In the subsequent step, carbocation **17** would undergo a nucleophilic attack at the silicon center by an alcohol to give the final products **4**−**11** and **13**−**15** after protonolysis of the C−Au bond. Despite the sterically hindered environment around the silicon center, presumably, the formation of a strong Si−O bond is the driving force to form the observed products. Although the formation of a putative carbenoid **18** followed by its alcoholysis is conceivable, products **19** or **20** were not observed.[13] A direct alcoholysis of the allyl moiety of **1** was observed when the allyl becomes a methallyl group, which is the consequence of preferential activation of the more electron-rich methallyl group over the alkyne by the catalyst, thereby giving product **21**.

The utility of this tandem bond-forming technology was further expanded by the ring-closing metathesis[14] of alkoxy hydroallylation products (Scheme 2). Silyl ethers **4c** and **4f**/**4g** could be cyclized by Grubbs complex **22**[15] to form 10- and 8-membered siloxanes **23**−**25** in good yields. Also, the cross metathesis[16] of **4i** with 4-penten-1-ol provided the cross metathesis product **26** in 42% yield as a mixture of *Z*/*E*-isomers.

Scheme 2. Ring-Closing and Cross Metathesis of Silyl Ethers



In conclusion, we have developed a gold-catalyzed tandem intramolecular allyl transfer reaction induced by an alcoholysis of alkynyl allyl silanes, which generates alkoxy vinyl silanes[17] in high yield and *Z*/*E*-selectivity. Synthetic application of this tandem bond-forming process will be reported in due course.

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Supporting Information Available: General experimental procedures and characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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