Stereoselective Synthesis of Vinylsilanes by a Gold(I)-Catalyzed Acetylenic Sila-Cope Rearrangement

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Received May 25, 2006; E-mail: fdtoste@uclink.berkeley.edu

Published on Web 08/15/2006

Recent advances have dramatically increased the utility of organosilanes and silanolates as reagents for metal-catalyzed cross-coupling reactions. The application of these reactions to stereo-selective olefin synthesis is contingent on efficient and selective methods for the construction of vinylsilanes. Metal-mediated stereoselective addition to allylkenes is commonly employed for this purpose. For example, trans-allylsililation of alkynes and cis-allylmetition of silylacetylenes allow for the stereoselective construction of 1,4-dienylsilanes in which the allyl group is trans to silicon. On the other hand, application of alkylationmetation reactions to the stereoselective synthesis of olefins substituted with the allyl group cis to silicon is rare. The gold(I)-catalyzed rearrangement of propargyl vinyl ethers, which is hypothesized to proceed through a cyclization-induced rearrangement, was recently reported. We envisioned that gold(I)-induced 6-endo-dig cyclization of acetylenic allylsilanes would initiate a related rearrangement and provide a method for the stereoselective synthesis of cis-1,4-dienylsilanes.

To this end, treatment of vinylsilane 3 furnished a mixture of silacycle 4a and vinylsilane 5a which slowly converted into 1,4-diene 2a (Table 1, entries 1–3). Changing the silver additive from AgSbF6 to AgBF4 resulted in improved selectivity for the formation of silacycle 4a without deterioration of reaction efficiency (entry 4). While changing the steric of the alcohol did not divert the reaction pathway from silacycle formation (entries 5–7), the use of phenol as a nucleophile completely reversed the selectivity in favor of vinylsilane 5e (entry 8).

With these conditions in hand, the substrate scope of the gold(I)-catalyzed rearrangement of more robust diphenylsilane 3 furnished a mixture of silacycle 4a and vinylsilane 5a which slowly converted into 1,4-diene 2a (Table 1, entries 1–3). Changing the silver additive from AgSbF6 to AgBF4 resulted in improved selectivity for the formation of silacycle 4a without deterioration of reaction efficiency (entry 4). While changing the steric of the alcohol did not divert the reaction pathway from silacycle formation (entries 5–7), the use of phenol as a nucleophile completely reversed the selectivity in favor of vinylsilane 5e (entry 8).

With these conditions in hand, the substrate scope of the gold(I)-catalyzed rearrangements was probed (Table 2). We were pleased to find that substitution at the acetylenic position (R1) of allylsilane I-catalyzed rearrangements was probed (Table 2). We were pleased to find that substitution at the acetylenic position (R1) of allylsilane 1a with catalytic amounts of cationic tri-tert-butylphosphinegold(I), in the presence of 3 equiv of methanol, furnished 1,4-diene 2a in 78% yield after 1 h at room temperature (eq 1). While this reaction provided a general route to 2,2-disubstituted-1,4-dienes, it failed to afford the desired vinylsilane. We surmised that gold(I)-induced 6-endo-dig cyclization of acetylenic allylsilanes would initiate a related rearrangement and provide a method for the stereoselective synthesis of cis-1,4-dienylsilanes.

In accord with this hypothesis, gold(I)-catalyzed rearrangement of more robust diphenylsilane 3 furnished a mixture of silacycle 4a and vinylsilane 5a which slowly converted into 1,4-diene 2a (Table 1, entries 1–3). Changing the silver additive from AgSbF6 to AgBF4 resulted in improved selectivity for the formation of silacycle 4a without deterioration of reaction efficiency (entry 4). While changing the steric of the alcohol did not divert the reaction pathway from silacycle formation (entries 5–7), the use of phenol as a nucleophile completely reversed the selectivity in favor of vinylsilane 5e (entry 8).

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A proposed mechanism involving $S_{N}2'$ addition of the allylsilane onto a gold(I)-complexed alkene to generate a gold-stabilized cation is outlined in Scheme 1.13 While $\beta$-stilbene fragmentation is generally faster than trapping of the cation,14 stabilization of 9 by back-bonding from gold(I) (i.e., resonance structure 10)15 allows for methanol addition to afford cyclic silane 11. On the other hand, when the relative rate of nucleophilic trapping is decreased, selective trapping occurs at silyl cation 12 to afford vinylsilane 13. Presumably, this is the case when the less nucleophilic phenol is used and when addition to the cation is sterically encumbered (Table 2, entries 17 and 19). Furthermore, an increase in the relative rate of $\beta$-stilbene fragmentation as a result of the steric clash of the methyl group and the silicon substituents accounts for the observation that $\alpha$-substituted allylsilane 6k affords only vinylsilane 8u (Table 2, entry 21).

The products of the gold(I)-catalyzed acetylenic sila-Cope rearrangement serve as useful reagents in a number of transformations. For example, palladium-catalyzed cross-coupling1 of vinylsilane 8h with ethyl 4-iodobenzoate produced trisubstituted olefin 14 in 60% yield (eq 2). Moreover, $\alpha$-allylated aldehyde 15 was prepared through a Tamao oxidation16 of 8h. Additionally, the silacycles can be viewed as latent vinylsilanes that can be revealed on treatment with a mild Lewis acid. This allowed for chemoselective cross-coupling reactions of arylbromide 16 to be performed, while the vinyl silane remained protected as the silacycle (eq 3). Reaction of 17 with 5 mol% of Sc(OTf)$_3$ generated vinylsilane 18, which was subjected to a second cross-coupling reaction to afford tri-substituted olefin 19.

In conclusion, a cationic gold(I) complex has been developed as a catalyst for the first transition-metal-catalyzed acetylenic sila-Cope rearrangement.17 The reaction allows for the stereoselective synthesis of vinylsilanes substituted with a wide range of functional groups. Furthermore, depending on the choice of nucleophile, either cyclic or acyclic vinylsilanes were produced. Both of these reagents can be employed for stereoselective synthesis of trisubstituted olefins through transition-metal-catalyzed cross-coupling reactions.

References
(9) Under identical conditions, (Ph)PdAuCl required 10 h to afford 72% yield of 8a. On the other hand, no reaction was observed on treatment of 1 with AgSbF$_6$, 10% AgSbF$_6/4$% PPh$_3$, PCl$_3$, or (PhCN)$_2$PdCl$_2$. Reaction of 3 with (Ph)PdAuClAgBF$_4$ gave 4a and 5a in 15 and 7% yield, respectively. No reaction was observed on treatment of 3 with AgSbF$_6$, AgBF$_4$, PCl$_3$, (PhCN)$_2$PdCl$_2$, or CuOTf.
(11) The allylic analogue of 61 (R$^1$ = Ph, R$^2$ = H) did not undergo the gold(I)-catalyzed reaction with methanol and gave a complex mixture with phenol at 50 °C.
(12) Deuterium labeling is consistent with protonation of a vinylgold intermediate (see Supporting Information).

JA0636800

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