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Preliminary communication

METAL-PROMOTED CYCLIZATION

VI*. PALLADIUM-CATALYZED CYCLIZATION VIA INTRAMOLECULAR ALLYLATION OF ALKENYLMETALS

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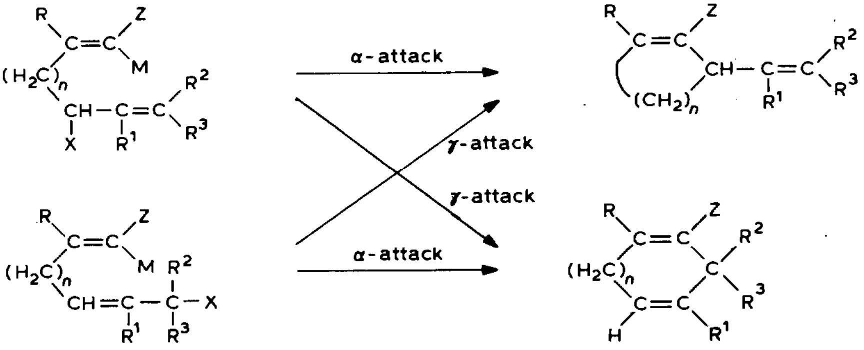
Summary

Treatment of silyl-protected terminal alkynes containing an allylic alcohol moiety with Me_3Al, $i\text{-}Bu_2AlH$, $ZnCl_2$, and a catalytic amount of $Pd(PPh_3)_4$, in this order, induces cyclization in cases where the reaction can lead to the formation of five-membered rings via either α- or γ-attack.

We have recently reported that the reaction of alkenyl- and aryl-metals containing Al or Zn with allylic electrophiles can be markedly catalyzed by phosphinepalladium complexes [2,3]. The intramolecular version of the reaction would provide an attractive route to cyclic alkenes (Scheme 1).



(R, R^1, R^2, or R^3 = H or C group. M = Al or Zn.
X = halogen or O group. Zn = H, SiR_3, etc.)

SCHEME 1

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[*] For part V see ref. 1.
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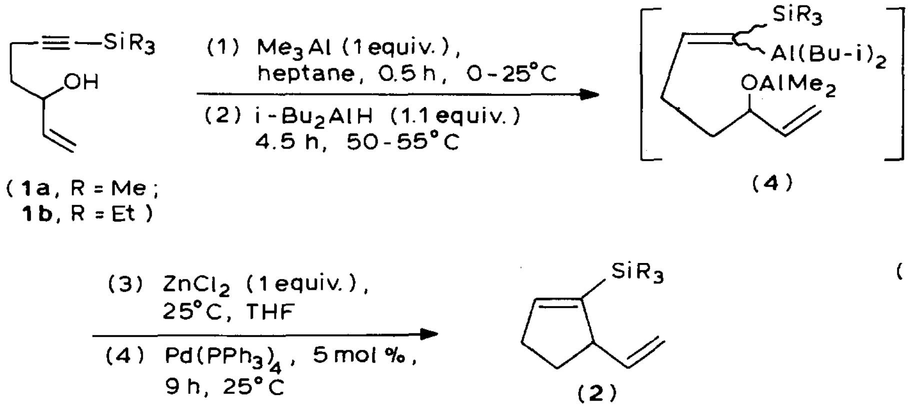
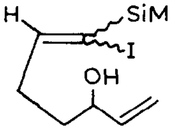
Although generation of the required alkenylmetals with proper stereochemistry in the presence of allylic electrophiles initially appeared to be difficult, we were encouraged by the following two recent findings. (i) A wide variety of allyl alcohol derivatives, including those containing OAc, $OPO(OEt)_2$, $OAlR_2$, and $OSiR_3$, participate in the Pd-catalyzed allylation [3a]. (ii) Although *cis*-hydrometallation or carbometallation of alkynes containing an allyl alcohol moiety would produce "wrong" stereoisomers, the presence of a silyl group in the terminal position of an alkyne leads to the formation of 1-silyl-1-alkenylmetals that can undergo *cis—trans* isomerization under relatively mild conditions [4].

We have indeed found that treatment of 7-trimethyl-2-hepten-6-yn-3-ol (**1a**) with Me_3Al in heptane (1 equiv, 0.5 h, 0—25°C), i-Bu_2AlH (1.1 equiv, 4.5 h, 50—55°C), $ZnCl_2$ in THF (1 equiv, 25°C), and $Pd(PPh_3)_4$ in THF (5 mol%, 9 h, 25°C), in this order, produces **2a** [5] in 55% yield (eq. 1). The reaction is indeed promoted by both $ZnCl_2$ [6] and $Pd(PPh_3)_4$, since no cyclization was observed in the absence of either of these two reagents.



(1)

After hydroalumination of **1a** with i-Bu_2AlH, quenching with iodine gave an alkenyl iodide (**3**) in good yield as a roughly 70/30 mixture of the *Z* and *E* isomers, supporting the intermediacy of **4a** in eq. 1.



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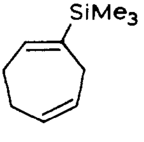

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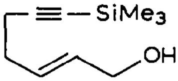
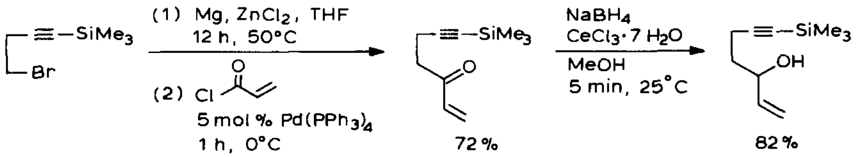


(6)

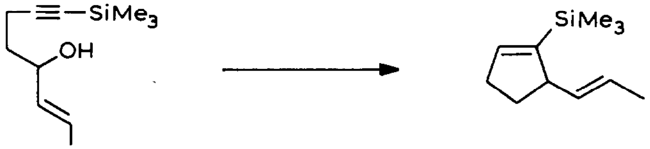
The required starting compound (**1a**) was obtained in 59% yield from 4-bromo-1-trimethylsilyl-1-butyne [7] via Pd-catalyzed acylation [8]—reduction [9] (eq. 2).



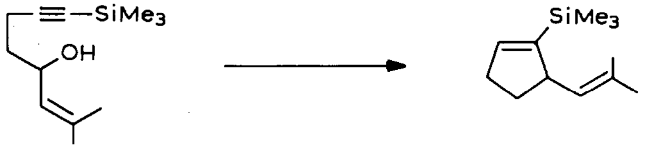
(2)

No detectable amount of the regioisomeric seven-membered ring product (5) was formed. Thus, the reaction is essentially 100% regioselective. However, the reaction is not regiospecific, since the regioisomeric starting compound (6) also produced 2a, uncontaminated by 5, in ca. 40% yield.

The preparation and cyclization of 7 and 8 were carried out as described for 1a to produce 9 (54%) [5] and 10 (52%) [5], respectively, in yields shown in parentheses (eqs. 3 and 4).



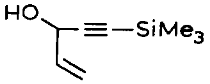
(7) (9) (3)



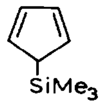
(8) (10) (4)

Although the cyclization yields are modest, the product region of the GLC (SE-30) traces of the reaction mixtures was clean, and the yield was apparently limited by the fact that the intermediate alkenylalanes were *E* and *Z* mixtures. Presumably, the desired cyclization takes place in the *E* configuration, in which the Al atom and the allylic moiety are *cis* to each other. We therefore hoped to attain a high *E*/*Z* ratio by incorporating a bulky silyl group, which should help force the allyl-containing group to be *trans* to Si [10] and hence *cis* to Al. We have tested this notion in one case and have indeed found that the triethylsilyl analog of 1a, i.e., 1b, indeed cyclizes to give 2b [5] in 75% yield. This improved procedure is yet to be applied to other cases but promises to provide a solution to the above-described yield problem.

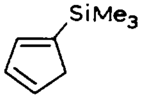
Treatment of 11 with Me_3Al, $i\text{-}Bu_2AlH$, $ZnCl_2$, $Pd(PPh_3)_4$, as described above, mainly produced 5-trimethylsilylcyclopentadiene (12) in 50% yield. Its spectral and chromatographic properties are identical with those of an authentic sample of 12 prepared by a known method [11]. Since 12 is known to be the major regioisomer ($\sim$85%) in a fluxional mixture containing two other regioisomers [12], the results are consistent with the initial formation of 13 which, in turn, could have arisen via 14.



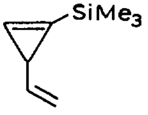
(11)



(12)

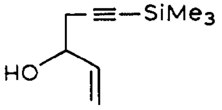


(13)



(14)

Quite unexpectedly, neither 15 nor 16 has yielded any significant amount of mono-cyclization product under the same conditions as described above. Thus, the current scope of this cyclization reaction is limited to the formation of five-membered rings. The origin of the ring-size specificity is not clear and is currently under investigation.



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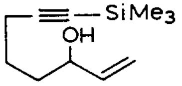

(16)

Although the results presented above need to be further improved, they do provide a novel entry in the rapidly growing list of the alkenylmetal cyclization reactions [13].

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