

INTRAMOLECULAR CYCLIZATIONS OF ALLYL- AND PROPARGYLSILANES

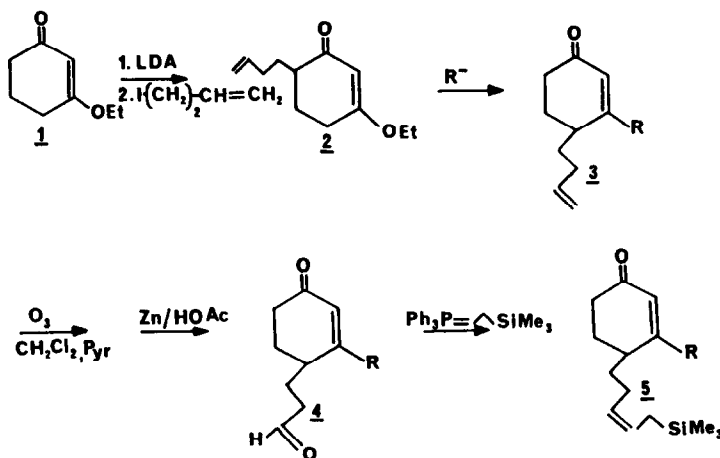
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Abstract: Allylsilanes of type 5 and propargylsilanes of type 13 undergo efficient cyclizations upon treatment with EtAlCl_2 in toluene to afford stereoselectively functionalized hydrindanones of type 6 and spiro[4,5]decanes of type 14.

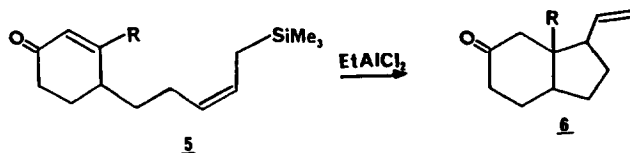
We have recently reported a new stereoselective route to functionalized spiroketones using Lewis acid-catalyzed cyclizations of allylsilanes.¹

In connection with other studies we required convenient syntheses of functionalized cis-fused hydrindanones and spiro[4,5]decanes containing the allene functionality. The synthesis for compounds 5 was carried out using 3-ethoxy cyclohexenone (1) as starting material, which was alkylated at -78°C with LDA as base. Treatment of 2 with either LiAlH_4 ,² MeLi or EtLi led to compound 3 which was selectively ozonized using Sudan Red as indicator.² Compound 4 yielded the desired allylsilane 5 after reaction with the Seyferth-Fleming ylid.³



R^- : a = LiAlH_4 ; b = MeLi; c = EtLi

We have found that allylsilanes 5 react smoothly with EtAlCl_2 in toluene at various temperatures to give functionalized hydrindanones 6 in a stereoselective way in good yields as shown in Table 1.⁴ G.Majetich and coworkers have published a similar reaction using fluoride ion in DMF/HMPT, but cyclization failed with more common Lewis acids like TiCl_4 or BF_3 ⁵ (see also reference 1). Very recently, Tokoroyama et al. have found a Sakurai reaction forming a decalone derivative with TiCl_4 as Lewis acid.⁶ These results clearly show that choice of Lewis acid is very important for the cyclization.



R: a = H; b = Me; c = Et

Interestingly, the reaction proceeds diastereoselectively favoring the more compact synclinal transition state 7 over the alternative 8. This fact is probably due to chelation control of the carbonyl group, the Lewis acid, and the silicon atom.⁷ A similar preference for analogous reactions of allylsilanes and allylstannanes with aldehydes via the synclinal geometry was observed by S.E. Denmark and coworkers.⁸

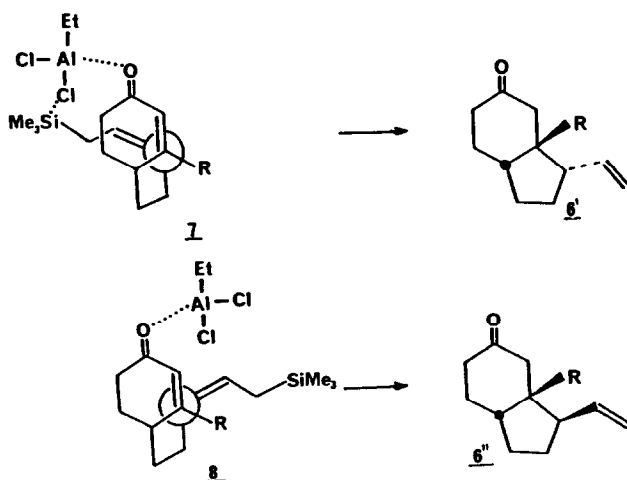


Table 1. Conditions for the Conversion 5 → 6, Ratio of the Diastereomers 6' and 6'', and Yields of 6 [a]

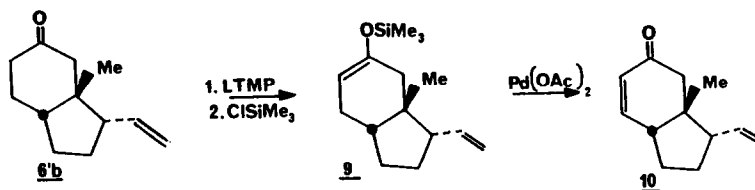
<u>5</u>	Conditions	<u>6'</u>	:	<u>6''</u>	Yield(%)*
a	toluene, 0°C	1	:	1	84
a	toluene, -78°C	4	:	1	92
b	toluene, 0°C	2	:	1	91
b	toluene, -30°C	3	:	1	77
b	toluene, -78°C	no reaction			
c	toluene, 0°C	2	:	1	86
c	toluene, -30°C	2,5	:	1	90
c	toluene, -78°C	no reaction			

* Kugelrohr distillation

[a] General procedure, e.g. for 6b. To a stirred solution of 1.82 g (7.26 mmol) of 5b in anhydrous toluene (100 ml) is added ethylaluminum dichloride (1.98 ml of a 1 : 1 solution in hexane) at 0°C. The mixture is stirred for 30 min at 0°C, treated with 50 ml of water, and the phases are separated and extracted twice with 80 ml of ether. The combined organic phases are dried (MgSO₄) and evaporated. The crude product was chromatographed with 5% ethylacetate/petroleum ether⁴ to yield 950 mg of analytically pure 6b (6'b:6''b=2:1).

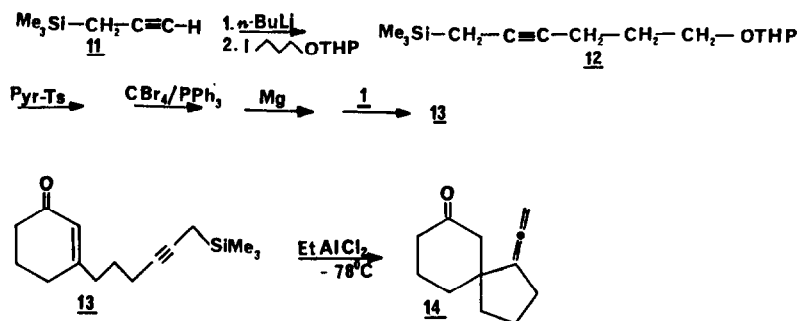
Physical data of 6'b: IR (film): 1710 (s), 900 (m) cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 0.97 (d, 3H, W-coupling, J = 0.71 Hz), 1.5-2.0 (m, 7H), 2.1-2.4 (m, 5H), 4.9-5.0 (m, 2H), 5.55-5.60 (m, 1H); ¹³C-NMR (100.61 MHz, CDCl₃): δ 212.70 (s, C-3), 137.44 (d, C-11), 116.04 (t, C-12), 55.91 (d, C-9), 48.41 (s, C-1), 44.52 (t, C-2), 44.46 (d, C-6), 36.24 (t, C-4), 27.40, 26.55, 25.50 (3 × t, C-5, C-7, C-8), 24.54 (q, C-10).

Compound 6'b was transformed to the enone 10 by regioselective deprotonation with LTMP (lithium tetramethyl piperidide) in THF at -78°C followed by quenching with TMSCl and subsequent reaction with Pd(OAc)₂⁹ to the desired enone 10.



Enone 10 represents a highly functionalized intermediate potentially useful for the synthesis of dendrobine.¹⁰ Further transformations, e.g. 1,4-additions are now in progress.

In addition compound 13 was cyclized to the spiro[4,5]decane 14. The synthesis was straight forward using propargylsilane as starting material.¹¹ Compound 11 was deprotonated with n-BuLi, and alkylated to yield 12. The THP ether was cleaved with pyridinium tosylate and the alcohol was transformed to the bromide. Subsequent reaction of the Grignard reagent with 1 yielded the desired material which cyclized at -78°C with EtAlCl₂ in 62% yield (after chromatography) to compound 14.¹²



Compound 14 represents again a functionalized intermediate which can be easily transformed into other useful precursors.

It is important to note that the same reaction works with optically active ene ketals. The details of that chemistry will be published in a forthcoming paper.

Acknowledgements

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References and Notes

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- IR (film): 1955 (s), 1710 (s) cm^{-1} ; $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ 1.3-2.6 (m, 14H), 4.80 (t, $J = 4.46$ Hz, 2H). $^{13}\text{C-NMR}$ (50.33 MHz): δ 211.00 (s), 202.36 (s), 110.84 (s), 78.56 (t), 52.36 (t), 49.22 (s), 40.99 (t), 37.68 (t), 38.85 (t), 30.34 (t), 23.64 (t), 22.92 (t).

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