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Regio- and Stereo-Selective Reactions of Trimethylsilyl-Substituted Allyl-Chromium Reagents with Aldehydes

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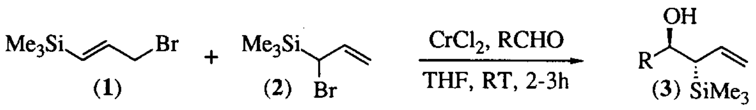
Abstract: *The use of the title compounds in the syntheses of anti-β-hydroxysilanes (3) and vinylsilanes (13-14) is described.*

Acyclic regio- and stereo-control using allyl-organometallics remains an important topic of research in organic chemistry.[1] Some of the most selective reactions have been observed with various substituted allyl-chromium reagents.[1a,2] We now communicate our preliminary results concerning the syntheses and reactions of the first silyl-substituted allyl-chromium reagents. Their syntheses do not require transmetallations from allyl-lithiums, and their reactions with aldehydes proceed under mild conditions to give new access to structures of previously demonstrated use in organic synthesis. The trimethylsilyl substituent imparts a strong regio- and stereo-chemical bias in the reactions examined.

We first reduced a 2:1 mixture of the allyl bromides (**1**) and (**2**), conveniently prepared by NBS allylic bromination of allyltrimethylsilane (44%),[3] with $CrCl_2$ in the presence of an aldehyde (Eq. 1).

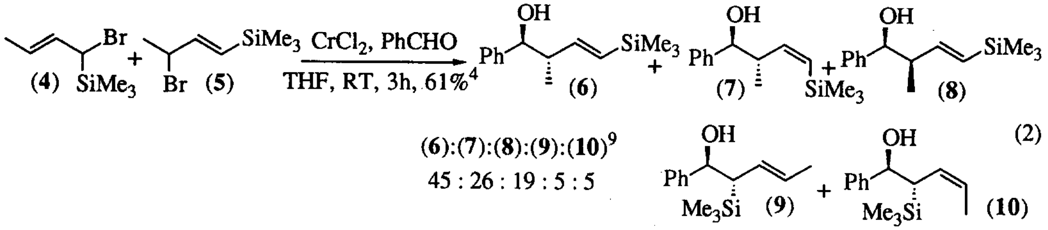


(1)

69% R = Ph, 54% R = C_3H_7, 65% R = cyclohexyl[4]

<u>Only</u> the *anti*-β-hydroxysilanes (**3**) were observed by high-field ^1H and ^{13}C nmr. Structural assignments were made by comparison with the literature, either directly (R = Ph and C_3H_7),[5] or after stereospecific KH-induced *Z*-diene formation (R = cyclohexyl).[6] The chemoselective nature of the reagent was indicated by a lack of reaction with acetophenone in THF or DMF. The same *anti*-β-hydroxysilane ((**3**), R = Ph) was obtained (76%) using $CrCl_2$, benzaldehyde and essentially pure allyl bromide (**2**), prepared by treating a mixture of allyl bromide and Me_3SiCl with LDA.[7] This provides further evidence that the bromides (**1**) and (**2**) react *via* the same *E*-allyl-chromium intermediate with an aldehyde in the usual chair transition state (R and Me_3Si equatorial). Convergence to this intermediate could occur on SET from $CrCl_2$ to the common allylic radical derived from bromides (**1**) and (**2**).[2]

Alkyl substitution resulted in a reversal of regioselectivity; vinylsilanes (**6**-**8**): *anti*-β-hydroxysilanes (**9**-**10**) 90:10 (Eq. 2).[8]

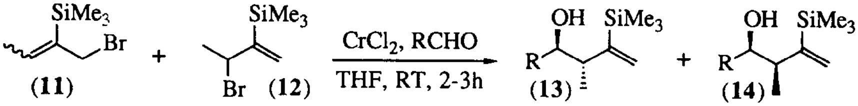


(6):(7):(8):(9):(10)[9]
45 : 26 : 19 : 5 : 5

(2)

The high regioselectivity may be explained by S_E2' attack by benzaldehyde on the (η^1-bound) organochromium intermediate having chromium at the less hindered (Si-substituted) end of the allyl system (C-Si longer than C-C).[1,2] For the vinylsilanes (**6**-**8**) *anti:syn* diastereoselection was 79:21, lower than that observed for the simple crotyl-chromium case (91:10),[2] whereas the preference for an equatorial trimethylsilyl group (to give the *E*-vinylsilanes (**6**, **8**)) in the presumed chair transition states was 71:29.

Finally, we examined the effect of trimethylsilyl substitution in the 2-position of a crotyl-chromium reagent (Eq. 3).[10]



(3)

91% R = Ph (33:67), 61% R = C_2H_5 (37:63)
57% R = $(CH_3)_2CH$ (32:68)[4,12]

Reversal of the *anti*-diastereoselectivity seen in the simple crotyl-chromium case is indicative of preferential *E*-geometry in the silyl-substituted crotyl-chromium intermediate, which results in an axial methyl substituent in the chair transition state with an aldehyde.[1a]

In summary, the reactions of trimethylsilyl-substituted allyl-chromium reagents with aldehydes provide useful routes to silyl-substituted homoallyl alcohols and, more generally, provide further information concerning the factors which influence regio- and stereo-control in the use of substituted allyl-organometallics. We are currently designing other functionalised allyl-chromium reagents based on our present results.

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