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ALLYLSILANES IN ORGANIC SYNTHESIS; CONVENIENT PREPARATION OF SYNTHETIC INTERMEDIATES BY CATALYTIC HYDROSILATION OF ACETYLENIC ALCOHOLS

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Summary : Synthetically useful vinylsilane-alcohols such as (1) can be easily prepared by the catalytic hydrosilation of the appropriate acetylenic alcohols in high yield, and with excellent regio- and stereoselectivity, without the need to protect the hydroxyl group.

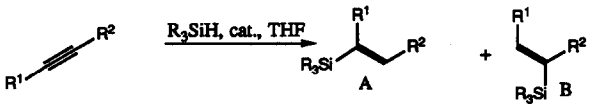
Vinylsilane-alcohols such as (1) are useful synthetic intermediates,[1] of particular interest to us is their use in the synthesis of chiral allylsilanes *via* Claisen rearrangement.[1a] The method which is generally used for the preparation of these vinylsilane-alcohols involves C-silylation of the appropriate acetylenic alcohol followed by stereoselective reduction of the silylated acetylenic alcohol.[1a,2]

(1)

X = NMe_2, OEt, OMe

Both these steps can prove troublesome. The direct silylation of the acetylenic alcohol can often produce mixtures of C- and O-silylated products,[3] necessitating further manipulations and/or separations. This is particularly wasteful if the more expensive silyl chlorides are used on a reasonable scale. The stereoselective reduction of the silylated acetylenic alcohol can be problematic in that mixtures of *cis*- and *trans*-vinyl silanes can be formed unless precise experimental conditions are used. Again this tends to be more of a problem as the scale is increased.[3] As we are interested in the preparation of chiral allylsilanes on a reasonable scale (>10g) we turned our attention to a method of preparation of this type of vinylsilane-alcohol by a direct route which would be amenable to scale-up. In this Letter we report the results of our recent work in this area.

Table 1[a]

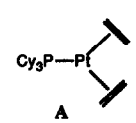


R^2 = Hydroxyl or carbonyl containing substituent

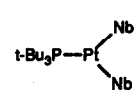
Alcohol	Silane (equiv.)	Catalyst	t (hr.)	Yeild[b]	A:B[c]	Conc.[d]
	$PhMe_2SiH$ (1.1)	A	2	82%	5.3:1	1
	n-Bu_3SiH (1.1)	A	8	84%	3.1:1	4
	Ph_3SiH (1.1)	A	36	54%	1.2:1	4
	$PhMe_2SiH$ (1.1)	B	1.5	88%	>95:5	1[e]
	Ph_3SiH (1.1)	B	1	67%	>95:5	4
	$PhMe_2SiH$ (1.1)	C	1.5	76%	>95:5	1
	$PhMe_2SiH$ (1.1)	A	20	96%	4.8:1	4
	$PhMe_2SiH$ (1.0)	B	3	70%	>95:5	4
	$PhMe_2SiH$ (1.1)	C	2.75	94%	12:1	4
	Ph_3SiH (1.0)	A	20	94%	>95:5	4
	$PhMe_2SiH$ (1.0)	A	24	98%	>95:5	4
	$PhMe_2SiH$ (1.0)	A	0.1	99%	>95:5	4
	$PhMe_2SiH$ (1.0)	A	6	75%	>95:5	2
	$PhMe_2SiH$ (1.0)	A	20	94%	4.2:1	4
	$PhMe_2SiH$ (1.1)	A	20	71%	1:2.5	4
	$PhMe_2SiH$ (1.0)	A	4	91%	1.1:1	4
	$PhMe_2SiH$ (1.0)	B	1	91%	1.3:1	4
	$PhMe_2SiH$ (1.0)	A	2	99%	2:1	4

[a]See text for typical experimental procedure; [b]Isolated yields; [c]By ^1H nmr; [d]Concentration (mmol ml^{-1}) of the silane; [e]Carried out on 50 mmol scale.

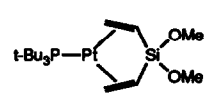
Catalysts-



A
Cy = Cyclohexyl



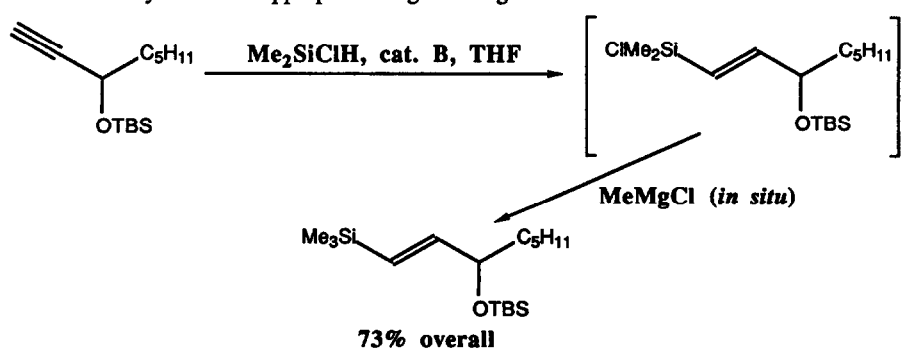
B
Nb = Norbornene



C
Ref. 4

For most synthetic applications we anticipate using the appropriate acetylenic alcohol as starting material since these are easily obtained and can be prepared in high enantiomeric purity *via* the enantioselective reduction of the acetylenic ketone.[5] We decided to investigate the direct hydrosilation of triple bonds catalysed by platinum complexes. This is well described for simple acetylenes,[6] and this reaction offers a number of significant advantages over other methods. The reaction generally provides an overall *cis*-addition of H-SiR_3 with the SiR_3 group being attached to the least hindered end of the triple bond.[6] In addition to being stereo- and regioselective, the reactions are often rapid and require only very low catalyst:substrate ratios (1:10^{-4} to 10^{-6}), and have advantages over the use of $H_2PtCl_6.6H_2O$.[6] In principle the direct hydrosilation of an acetylenic alcohol should require only one equivalent of silane,[7] assuming that the OH group does not become involved in the reaction, which can provide an economic advantage which is increased since the silanes are considerably cheaper per mole than the corresponding chlorosilanes.[8] At the low catalyst:substrate ratios typical of these reactions (*vide supra*) the cost of the catalyst per mole of product becomes small. *In view of these considerations we were gratified to find that the presence of the hydroxyl group in the acetylenic alcohols which we used as reactants did not interfere with the platinum-catalysed hydrosilation, and that excellent yields and selectivities can be obtained.* A representative selection of some of our results are shown in Table 1. These reactions are very easy to carry out, and appear to be sensitive to the steric demands of all of the reactants (including the catalyst). As far as we can measure by careful 300 MHz ^1H nmr spectrometry the products are the E-isomers of the vinylsilanes (i.e. *cis*-addition of H-SiR_3). On the whole, catalyst B appears to produce the highest regioselectivity which is consistent with a simple steric model for the reaction since this contains the bulkiest phosphine. Poor regioselectivity is observed with all catalysts when the acetylene has similar sized groups at each end, and when substantial electronic factors are present (as with methyl propiolate). Even in these cases where the regioselectivity is low, this approach does provide easy access to the vinylsilanes since the yields are high and in all cases studied by us the two regioisomers can be separated by flash column chromatography.

The direct introduction of the trimethylsilyl group would be complicated by the need to use trimethylsilane, but this limitation is easily overcome by using chlorodimethylsilane in the hydrosilation step followed by *in situ* reaction of the product with methyl magnesium chloride as shown below. This approach would also provide access to other silanes by use of the appropriate Grignard reagent.



73% overall

In conclusion we believe that the catalytic hydrosilation methodology described here is one of the most convenient methods for the preparation of stereochemically homogeneous vinyl silanes containing hydroxyl substituents.

Typical Experimental procedure:- The platinum complex B (8.7 mg, 0.015 mmol) was added in one portion to a well stirred, cooled (0°) solution of propargyl alcohol (2.698g, 48.1 mmol) and dimethylphenylsilane (7.22g, 52.95 mmol) in THF (55 ml) (**CARE**; efficient cooling and stirring as the reaction can be exothermic). The reaction mixture was then brought to reflux over 10 min (oil bath) and kept at reflux for 1.5 hr. The solvent was removed (rotary evaporator) and flash column chromatography (ethyl acetate/petrol 1:9) gave 1-dimethylphenylsilyl-3-hydroxypropene (8.29g, 88%). In this case the catalyst:substrate ratio was *ca.* 3200:1, on larger scale reactions there is no doubt that this could be increased further.

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8. For example, catalogue price per mole from Aldrich as 25g lots; $PhMe_2SiH$ - £73-60; $PhMe_2SiCl$ - £249-93.

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