Tetrahedron Letters,Vol.23,No.5,pp 557-560,1982 0040-4039/82/050557-04$03.00/0
Printed in Great Britain

REGIO- AND STEREOSELECTIVE SYNTHESIS OF ALLYLSILANES USING (METHYLPHENYLAMINO)TRIBUTYLPHOSPHONIUM IODIDE

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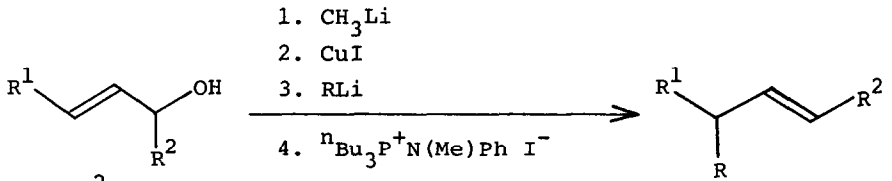
Regio- and stereoselective synthesis of variously substituted allylsilanes is achieved by organocuprate-mediated γ-coupling of allylic alcohols using the title reagent (1).

Recently, allylsilanes are recognized to be valuable synthetic intermediates[1], and a number of methods for the synthesis of allylsilanes have been explored[1,2]. However, the problem of regio- and stereocontrol still remains except for some special cases. Therefore, further development of highly regio- and stereocontrolled means are required to reply to its synthetic potentiality. We now wish to report a new general method, which has the virtue of being applicable to the preparation of variously substituted allylsilanes. The method is schematized by the transformation sequence as shown in eq 1.



2 3 (1)

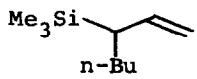
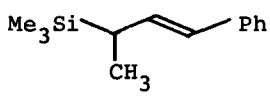
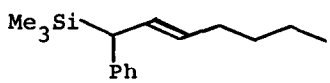
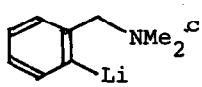
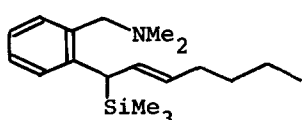
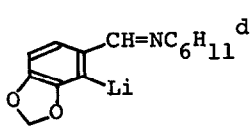
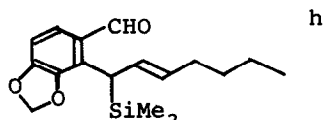
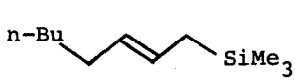
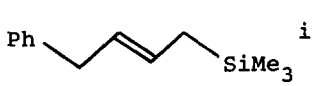
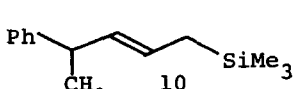
(1)

R^1=$SiMe_3$ or R^2=CH_2SiMe_3

The starting substrates, α-trimethylsilylmethyl[3] (2, R^2=CH_2SiMe_3) and γ-trimethylsilyl (2, R^1=$SiMe_3$) substituted allylic alcohols[4] (2) can be readily prepared in large quantities by conventional methods. Therefore, the direct alkylation of such alcohols (2) with organolithium compounds with the aid of (methylphenylamino)tributylphosphonium iodide (1)[5] would give an efficient method for the synthesis of allylsilanes. The full scope of the reaction is summarized in the Table.

This method has proven to be valuable in some aspects. (1) The reaction can be accomplished under mild conditions (-70°C∿room temperature). (2) The reaction is quite general and various substituted allylsilanes are directly prepared from substrate 2 in moderate yields with high regio-(S_N2' alkylation)

Table. Synthesis of Allylsilanes from the Reaction of Allylic Alcohols (2) with Organolithium Compounds Using 1[a]

Entry	Substrate (2) R^1	R^2	Organolithium Compound (RLi)[b]	Allylsilane (3)[6,e,f]	Isolated Yield[j,k] (%)
1	Me_3Si	H	n-BuLi		77[l]
2	Me_3Si	Ph	MeLi	 4	70
3	Me_3Si	n-Bu	PhLi	 5	55
4	Me_3Si	n-Bu		 6[7]	50
5	Me_3Si	n-Bu		 7[8]	49
6	H	Me_3SiCH_2	n-BuLi	 8	76
7	H	Me_3SiCH_2	PhLi	 9	53
8	Ph	Me_3SiCH_2	MeLi	 10	75

[a] All reactions were performed on a 3-6 mmol scale with the same procedure as described in the text. [b] One equivalent of organolithium compound was used. [c] Prepared by the literature: K. P. Klein and C. R. Hauser, J. Org. Chem., 32,

1479 (1967). [d] Prepared by the literature: F. E. Ziegler and K. W. Fowler, ibid., 41, 1564 (1976). [e] All products have been fully characterized by spectral means and elemental analyses. [f] Isomeric purity is higher than 99% by GLC. [g] 7-Trimethylsilylundec-5-ene 11 was obtained in 10% yield. [h] Compound 11 was obtained in 6% yield. [i] E/Z=2/1 (by GLC). [j] Pure substances by column chromatographic separation (silica gel). [k] In all reactions, starting alcohols 2 were recovered in 5-15%. [l] Isolated yield by Kugelrohr distillation, T_{bath} 104°C/58 mmHg.

and stereoselectivity (E-configuration of double bond). (3) This method is applicable to various organolithium compounds. Therefore, the reaction leads to an easy and straightforward access to variously functionalized allylsilanes. Thus, the introduction of 1-trimethylsilylhept-2-enyl group into the ortho-positions of N,N-dimethylbenzylamine and piperonal can be achieved by the reactions of 1-trimethylsilylhept-1-en-3-ol with the corresponding o-lithiated compounds regio- and stereoselectively (entries 4 and 5).

The preparation of 2-(1'-trimethylsilylhept-2'-enyl)piperonal is representative (entry 5). All procedures were performed under N_2 atmosphere. A green solution of the allyloxycopper was prepared from 1-trimethylsilylhept-1-en-3-ol (0.932 g, 5 mmol), MeLi (1.44 M in ether, 5.25 mmol), and cuprous iodide (0.952 g, 5 mmol) in dry THF (20 mL) at 0°C. In a separate flask, an orange suspension of o-lithiated piperonal cyclohexylimine was prepared by the treatment of piperonal cyclohexylimine (1.388 g, 6 mmol) with n-BuLi (1.6 M in hexane, 6.3 mmol) in dry THF (30 mL) at -70°C. To an orange suspension of the lithium (allyloxy)arylcuprate, which was prepared by the transfer of the o-lithiated compound to the allyloxycopper, was added a solution of 1 (2.167 g, 5 mmol) in dry DMF (20 mL) at -70°C. The mixture was stirred for 8 hr at -70°C to room temperature and quenched with a saturated aqueous NH_4Cl solution (0°C). After shaking of the ethereal extracts with 2N HCl aqueous solution (40 mL x 4) to remove N-methylaniline and to complete the hydrolysis of the imine, the solvent was removed in vacuo. Column chromatography followed by preparative tlc on silica gel gave the desired allylsilane[8] (0.778 g, 49% isolated yield based on the used alcohol; EtOAc-hexane 1:9, R_f 0.63).

The direct silylation of allylic alcohols (2: R^1,R^2=H, alkyl, and/or aryl) with trimethylsilyllithium using 1 is an alternative attractive method for the synthesis of allylsilanes. However, the regioselectivity for the silylation is not satisfactory. Thus, the treatment of 1-phenylprop-2-en-1-ol with trimethylsilyllithium under nitrogen gave an 1:1 mixture of 1-phenyl-3-trimethylsilylprop-1-ene and 3,3-trimethylsilylphenylprop-1-ene in 60% total yield. Therefore, for the silylation of allylic alcohols the Calas method[9]

which involves the reductive silylation of 2-alkenyloxysilanes with chlorotrimethylsilane and lithium is much superior to the silylation using 1.

Work is currently in progress on the application of this reaction to other synthesis of useful functionalized allylsilanes.

References and Notes

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3. 1,2-Addition of trimethylsilylmethylmagnesium chloride to α,β-unsaturated carbonyl compounds, see: M. J. Carter and I. Fleming, Chem. Comm., 679(1976).
4. Reduction of 3-trimethylsilylpropargylic alcohols with $LiAlH_4$, see: G. Stork, M. E. Jung, E. Colvin, and Y. Noel, J. Am. Chem. Soc., 96, 3684(1974).
5. Y. Tanigawa, H. Ohta, A. Sonoda, and S.-I. Murahashi, ibid., 100, 4610(1978).
6. The stereochemistry of allylsilanes except for 4 was characterized by the coupling constant of olefinic protons ($J_{transCH=CH}$, Hz) in the ^1H NMR and by the out-of-plane deformation vibration of trans-disubstituted olefins (cm^{-1}) in the IR as follows: 5, 15 Hz, 963 cm^{-1}; 6, 15, 965; 7, 16, 965; 8, 18, 965; E-9, 19, 965; 10, 19, 963. E-Stereochemistry of 4 was determined by the similar pattern of olefinic protons in the ^1H NMR with that of reported allylsilanes[2g] and by the IR as follows: δ (chemical shift from Me_3Si group as 0.00 ppm) 6.10-6.27 (m, 2H), 965 cm^{-1}.
7. TLC on silica gel, EtOAc-hexane 1:9, R_f 0.41. NMR(CCl_4,δ): 0.00(s, 9H), 0.91 (m, 3H), 1.15-1.60(m, 6H), 2.19(s, 6H), 3.48(d-d, 8, 1Hz, 1H), 3.24(s, 1H), 3.34(s, 1H), 5.23(d-t-d, 15, 6, 1Hz, 1H), 5.70(d-d-t, 15, 8, 1Hz, 1H), 7.06 (s, 4H).
8. NMR(CCl_4,δ): 0.00(s, 9H), 0.95(m, 3H), 1.10-1.60(m, 4H), 1.75-2.25(m, 2H), 4.58(d-d, 10, 1Hz, 1H), 5.33(d-t-d, 16, 6, 1Hz, 1H), 6.13(d-d-t, 16, 10, 1Hz, 1H), 5.95(d, 2Hz, 1H), 6.00(d, 2Hz, 1H), 6.63(d, 8Hz, 1H), 7.18(d, 8Hz, 1H), 9.88(s, 1H).
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(Received in Japan 29 October 1981)