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ALLYLSILANES FROM ALLYLCHLORIDES AND SILYLCUPRATES

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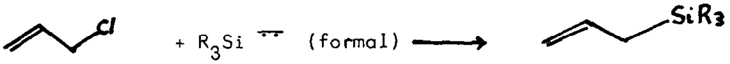
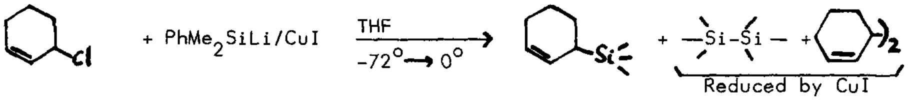
ABSTRACT: The beneficial effects of copper (I) salts on the reactions of cyclohex-2-enyl chlorides and 3,4-epoxycyclohexene with phenyldimethylsilyllithium are reported.

General procedures that exhibit a high level of stereo- and regiochemical control in the formation of allylsilanes are necessary for the continuing exploitation of these silanes in synthesis.[1,2] The formation of such silanes from allylic halides and (formal) silylanions[3] has the virtues of directness and promise of such control if "nucleophilic" characteristics can be conferred on the silyl reagent.[4]

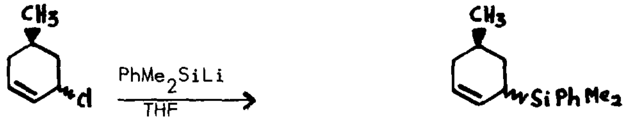


Our interest in such halide displacement by organometalanionoids[5] prompted examination of the silylation of certain allylchlorides by phenyldimethylsilyllithium in the presence of Cu(I) salts, in anticipation that a "nucleophilic" silyl group would be transferred from the presumed silylcuprate species with accompanying regio and stereocontrol. We chose $PhMe_2SiLi$ (and to a lesser extent, $Ph_2MeSiLi$) for study, as in contrast to Me_3SiLi, these reagents are readily prepared in tetrahydrofuran,[6] thus avoiding the use of hexamethylphosphorictriamide.

Cyclohex-2-enylchloride, on reaction with $PhMe_2SiLi$ (50% excess; THF; $-72^\circ \rightarrow 0^\circ$) in the absence of Cu(I), yielded the allylsilane[7] and bicyclohexenyl in a ratio of 70:30, together with disilane (GC-MS analysis). However, addition of 0.5 equivalent of CuI to the $PhMe_2SiLi$ (-78°; stirring) prior to addition of cyclohex-2-enylchloride, greatly suppressed bicyclohexenyl formation, now 7:93 with respect to the target silane (75% isolated yield). Disilane production was also markedly reduced, consistent with bicyclohexenyl and disilane both resulting in part, from chloro-lithium exchange followed by coupling.



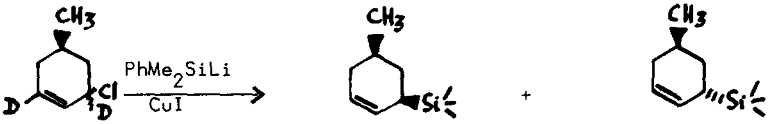
The stereochemistry of chloride displacement was examined with cis and trans-5-methylcyclohex-2-enyl chlorides,[8] and the use of CuI significantly improved the stereoselectivity of chloride displacement, to the extent of apparent stereospecific inversion.



cis:*trans*	*cis*:*trans*		
81:19	54	46	20:80
13:87	72	28	85:15
	No CuI		Added CuI

(The configurations of the product silanes were established by ^{13}C, ^{29}Si and ^{1}H nmr spectra following procedures described elsewhere[8(b)] and pure samples were obtained by preparative VPC. $\delta_{^{29}Si}$ at -2.47 ppm *(cis)* and -2.56 ppm (*trans*)).

The regiospecificity of this apparently stereospecific displacement was examined with ^{2}H labelled 5-methylcyclohex-2-enyl chloride[8] as shown below, with ^{2}H distributions measured by direct ^{2}H nmr spectroscopy.

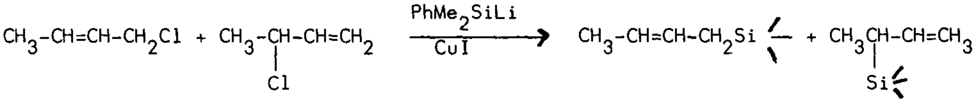


cis:*trans* = 15:85

ca 80% *ca* 20%

$\frac{\text{Allyl-}^2\text{H}}{\text{Vinyl-}^2\text{H}} = \frac{82}{18}$ $\frac{\text{Allyl-}^2\text{H}}{\text{Vinyl-}^2\text{H}} = \frac{30}{70}$

The interesting result is that despite the apparent stereospecific formation of silane, extensive allylic relocation of ^{2}H occurs, implying predominant *anti*-S_N2' introduction of the silyl moiety.[9] Allylic rearrangement is very substantial in reactions of α-methallyl and crotyl chlorides (below),[10] with silylation of the butenyl-Grignard[11] (from predominantly α-methallylchloride; THF; reflux) providing chiefly α-methylallylsilane, a distribution resembling that for trimethylsilylation.[2(c)]

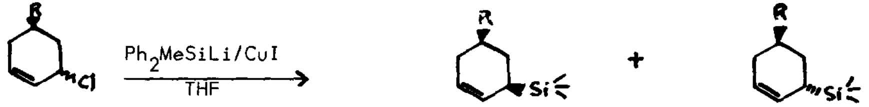


$$\mathrm{CH_3\text{-}CH{=}CH\text{-}CH_2Cl + CH_3\text{-}\underset{Cl}{CH}\text{-}CH{=}CH_2 \xrightarrow[CuI]{PhMe_2SiLi} CH_3\text{-}CH{=}CH\text{-}CH_2Si + CH_3\underset{Si}{CH}\text{-}CH{=}CH_3}$$

<10	>90	65/31 = E/Z	4
85	15	56/15	29
"CH_3-CH=CH-CH_2MgCl"	$\xrightarrow[THF]{PhMe_2SiCl}$	45 (E/Z ∿ 1/1)	55

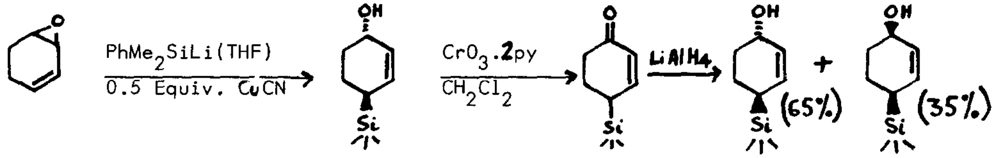
(The α-methylallylsilane above, shows dual Si-$\underline{CH_3}$ in the ^{13}C spectrum at -5.49 and -5.05 ppm, with E-2-butenylsilane at -3.42 and the Z-isomer at -3.32 ppm, with $\delta_{^{29}Si}$ at -2.13, -4.57 and -3.76 ppm respectively).

Stereospecific chloride displacement in the cyclohex-2-enyl system by diphenylmethylsilyllithium-CuI was also observed, as shown below.



	cis:*trans*		
R=CH_3	15:85	85 ($\delta_{^{29}Si}$ = -7.70 ppm)	17 ($\delta_{^{29}Si}$ = -7.92 ppm)
	75:25	23	77
R=$(CH_3)_3C$	15:85	83 ($\delta_{^{29}Si}$ = -7.50 ppm)	17 ($\delta_{^{29}Si}$ = -8.88 ppm)

In an approach to functionalised allylsilane synthesis, the reaction between the mixed cyanocuprate $[PhMe_2SiCuCN]Li$ towards 3,4-epoxycyclohexene was examined, following the reports of Marino and co-workers on alkylcyanocuprates.[12] This sequence provided essentially a single isomer (>75% based on epoxide) on the basis of the ^{13}C nmr spectrum. The ^{1}H ($>C<^{H}_{OH}$, $W_{\frac{1}{2}}$ ~14 Hz)), and ^{13}C nmr spectra indicated the *trans*-4-(phenyldimethylsilyl)cyclohex-2-enol structure, which was confirmed by oxidation to 4-(phenyldimethylsilyl)cyclohex-2-enone[13] and reduction to a mixture of alcohols,[14] with the major component (anticipated to be *trans*) being identical with the single isomer formed directly. The use of CuI was far less attractive for achieving this conversion, as a mixture of products in lower yield resulted.



Additional aspects of the formation of allylic silanes by these procedures are being studied as well as details of their transformations.

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REFERENCES AND NOTES:

1. See, for example, H. Sakurai, Pure and Appl. Chem., 54, 1 (1982); E. Colvin, Silicon in Organic Synthesis, Butterworths, London, 1981.
2. For some recent allylsilane syntheses see: (a) Y. Tanigawa, Y. Fuse and S. Murahashi, Tetrahedron Lett., 557 (1982); (b) E. Negishi, F. Luo and C.L. Rand, Tetrahedron Lett., 27 (1982); (c) A. Hosomi, H. Iguchi and H. Sakurai, Chemistry Lett., 223 (1982), (d) C.N. Hsiao and H. Shechter, Tetrahedron Lett., 1963 (1982); (e) C. Biran, J. Dunoguès, R. Calas, J. Gerral and T. Tskhovrebachvili, Syntheses, 220 (19810.
3. Recently the conversion of geranylchloride to the Me_3Si-derivative was reported,[2(b)] (Me_3SiLi; 81%) whereas silylation of allylchloride with Me_3SiLi(HMPA) resulted in very low conversion (7%), and CuI was essential for an acceptable yield. (J.G. Smith, N.R. Quinn and M. Viswanathan, Synthetic Comm., 13, 1 (1983). Our attempt to silylate cyclohex-2-enylacetate with $PhMe_2SiLi$-CuI produced a number of products, with none of the desired allylsilane being identified. See also I. Fleming & D. Marchi, Synthesis, 560 (1981).

4. R_3SiM reagents could be envisaged to demonstrate a variety of capabilities towards alkyl halides, including e-transfer, halo-M exchange, base etc., in addition to formal "S_N2" behaviour. For example see T. Hiyama, M. Obayashi, I. Mori and H. Nozaki, J. Org. Chem., 48, 914 (1983).
5. W. Kitching, K. Harvey and H.A. Olszowy, J. Org. Chem., 47, 1893 (1982).
6. D.J. Alger, I. Fleming and S.K. Patel, J. Chem. Soc., Perkin Trans I., 2520 (1981).
7. ^1H nmr (300 MHz): δ0.27, 0.28 ($Si(CH_3)_2$); 1.35-2.1 (7H); 5.63 (narrow "AB", 2H, J_{AB} ∿12 Hz; 7.3-7.5 (5H). ^{13}C nmr: δ-4.68, -4.81, 22.54, 25.02, 23.83, 25.61, 125.88, 127.47. $\delta_{^{29}Si}$ = -2.54 ppm. See also Y. Okuda, M. Sato, K. Oshima and H. Nozaki, Tetrahedron Lett., 2015 (1983).
8. (a) H.L. Goering, T.D. Nevitt and E.F. Silversmith, J. Am. Chem. Soc., 77, 4042 (1955) and subsequent papers, (b) G. Wickham, D. Young and W. Kitching, J. Org. Chem., 47, 4884 (1982).
9. This result is similar to some observations on allylic alkylation in this system by certain alkylcuprate species. See H.L. Goering and V.D. Singleton, J. Am. Chem. Soc., 98, 7854 (1976) and subsequent reports, especially H.L. Goering and S.S. Kantner, J. Org. Chem., 46, 2144 (1981). The reaction of a *cis,trans* mixture (27:73) of 3,5-dimethylcyclohex-2-enyl chlorides provided (in low yield) a mixture of the unrearranged *cis* (70%) and *trans* (30%) 3,5-dimethylcyclohex-2-enyl(phenyldimethyl)silanes. $\delta_{^{29}Si}$ = -2.41 ppm (*cis*) and -2.50 ppm (*trans*). The low yield may be associated with reluctance to form the (tertiary) allylic copper complex, its more rapid decomposition, or allylic isomerisation. See H.L. Goering and V.D. Singleton, J. Org. Chem., 48, 1531 (1983).
10. Triphenylsilyllithium converts E and Z-but-2-enyl chlorides to the corresponding but-2-enyl silanes (100%) without loss in double bond configuration, whereas 3-chloro-1-butene yields a mixture of the three butenylsilanes. See E. Matarasso-Tchiroukhine and P. Cadiot, J. Organometal. Chem., 121, 155 (1976).
11. "Butenyl-Grignard reagent" is described in terms of an equilibrium between the but-2-enyl (crotyl) and α-methylallyl structures, with the former heavily predominating. See J.E. Nordlander, W.G. Young and J.D. Roberts, J. Am. Chem. Soc., 83, 494 (1961).
12. J.P. Marino and H. Abe, Synthesis, 872 (1980).
13. ^1H nmr (300 MHz): δ0.40; 0.41 ($Si(CH_3)_2$); δ2-2.30 (5H) (cycloalkyl); δ5.97 and δ6.97 (2H, vinyl). ^{13}C nmr: -4.13; -3.90 ($Si(CH_3)_2$); 23.51, 29.24, 36.65, 129.67, 153.42, 199.07. ^{29}Si nmr: -1.67 ppm. IR: 1690 cm^{-1} ($\nu_{C=O}$).
14. These alcohols were completely characterised by ^1H, ^{13}C and ^{29}Si nmr. The chief features were: ^1H nmr: δ0.28; 0.29 ($Si(CH_3)_2$, *trans*); δ0.32; 0.31 ($Si(CH_3)_2$, *cis*); $>C\!<^{H}_{OH}$ δ4.10 (*trans*); 4.07 (*cis*). (Very similar shifts for $>C\!<^{H}_{OH}$ are observed in *trans* (δ4.15) and *cis* (δ4.10)-4-methylcyclohex-2-enol). ^{13}C nmr: *trans*: -4.78, -4.61 ($Si(CH_3)_2$); 20.22, 26.05, 31.75, 65.77 (C-O), 129.05, 130.66. *cis*: -4.93, -4.73 ($Si(CH_3)_2$); 18.93, 26.12, 31.19, 64.21 (C-O), 129.10, 131.98. ^{29}Si nmr: -2.47 ppm (*trans*); -2.34 ppm (*cis*).

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