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# SILYL-CUPRATION OF ALLENE. A NEW ROUTE TO SILYLATED SYNTHONS

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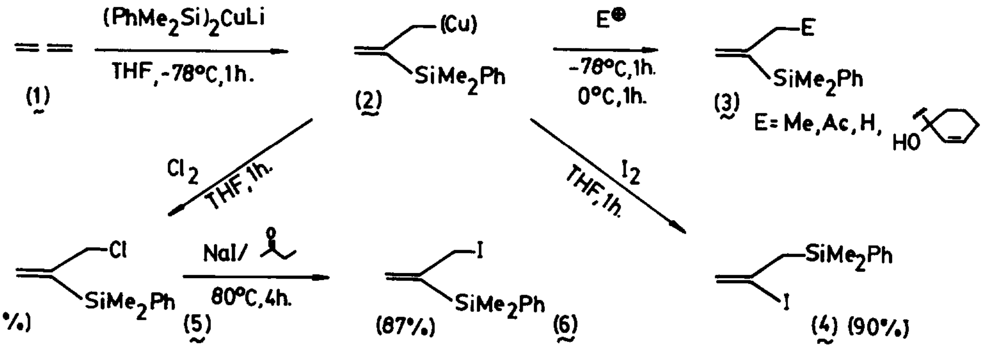
Abstract. Silyl-cupration of allene followed by treatment with iodine anomalously gives the vinyl iodide 4, a versatile synthetic intermediate.

Recently, we reported the synthesis of allylsilanes and vinylsilanes by silyl-cupration of allenes with lithium bis(phenyldimethylsilyl)cuprate.[1] Whether allyl- or vinylsilanes were formed depended upon the degree of substitution of the allene. With allene itself (1), lithium bis(phenyldimethylsilyl)cuprate, prepared from phenyldimethylsilyl-lithium and copper(I) cyanide,[2] gave a silylated allyl-copper intermediate 2, which reacted with electrophiles (methyl iodide, acetyl chloride and cyclohexenone) to give the vinyl silanes 3[1] (Scheme 1).



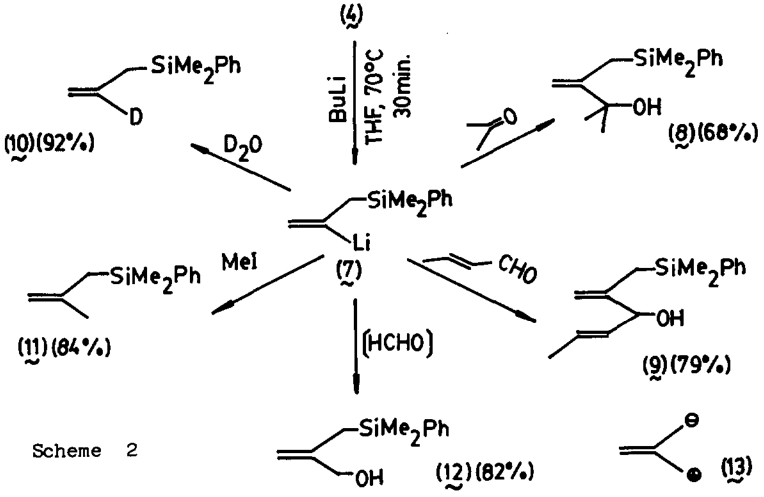
Scheme 1

Surprisingly, we now find that the reaction of the same intermediate with iodine (THF, -70ºC, 1h), does not give the vinylsilane but gives instead the allylsilane 4[3], whereas chlorine behaves like the other electrophiles and gives the vinylsilane 5[3]. On the other hand, 5 reacts with sodium iodide to give the expected allyl iodide 6[3].

Whatever the reason for this remarkable change in regiochemistry, the vinyl iodide 4 is a versatile synthetic intermediate; it can be lithiated by metal-iodine exchange (n-BuLi, -70ºC, 30 min), and the resulting silylated $C_3$-nucleophile 7 reacts cleanly with acetone and crotonaldehyde (-30ºC, 2 h) to give the silylated alcohols 8[3] and 9[3], after quenching ($NH_4Cl$ aq)(Scheme 2). The anion 7 can also be deuterated ($D_2O$) or alkylated to give 10[3] and 11[3] respectively (Scheme 2).

Compounds analogous to 8 are useful intermediates in the synthesis of 9,10-didehydronorzizaene derivatives,[4] and the trimethylsilyl analogue of 12 has been used as a $C_4$ synthon 13 in much synthetic work by Trost and his co-workers.[5] The present route is an easy entry into these powerful synthetic methods.

It seems likely that the change of regiochemistry may be a consequence of reversibility in the silyl-cupration, for which we already have evidence.[1]



Scheme 2

## References

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3. 3(E=H): $R_F$(hexane)=0.4. IR(film): 1609, 1253, 1124 $cm^{-1}$. $^1H$-NMR($CDCl_3$): δ 7.4-7.75 (m, 5H), 5.75 (m, 1H), 5.42 (m, 1H), 1.9 (d, J=1.3 Hz, 3H), 0.44 (s, 6H). $^{13}C$-NMR: δ -3.42 (Me-Si), 22.56 (Me-C=), 126.60 ($H_2C=$), 127.85, 129.02, 133.98 (Ar CH groups), 139.17 (Ar quaternary C), 146.17 (olefinic quaternary C). MS: m/e=176 ($M^+$, 21%). 4: $R_F$(hexane)=0.34. Calc., C, 43.72; H, 5.00; found:C, 43.84; H, 5.08. IR(film):1606, 1260, 1123 $cm^{-1}$. $^1H$-NMR($CDCl_3$): δ 7.4-7.7 (m, 5H), 5.72 (d, J=1.2 Hz, 1H), 5.59 (d, J=1.2 Hz, 1H), 2.55 (s, 2H), 0.5 (s, 6H). $^{13}C$-NMR: δ -2.88 (Me-Si), 31.09 ($CH_2$-C=), 104.65 (olefinic quaternary C), 127.27 ($H_2C=$), 127.87, 129.08, 133.80 (Ar CH groups), 138.98 (Ar quaternary C). 5: $R_F$(pentane)=0.37. Calc., C, 62.68; H, 7.17; found: C, 62.89; H, 7.27. $^1H$-NMR($CDCl_3$): δ 7.4-7.7 (m, 5H), 5.6 (d, J=1.1 Hz, 1H), 5.5 (d, J=1.1 Hz, 1H), 4.35 (s, 2H), 0.45 (s, 6H). $^{13}C$-NMR: δ -2.72 (Me-Si), 49.13 ($CH_2$-Cl), 130.07 ($H_2C=$), 128.08, 129.35, 134.03 (Ar CH groups), 138.89 (Ar quaternary C), 145.45 (olefinic quaternary C). 6: $R_F$ (pentane)=0.36. Calc., C, 43.72; H, 5.00; found:C, 43.78; H, 5.12. $^1H$-NMR($CDCl_3$): δ 7.4-7.8 (m, 5H), 6.32 (d, J=1.2 Hz, 1H), 5.91 (d, J=1.2 Hz, 1H), 3.5 (s, 2H), 0.45 (s, 6H). $^{13}C$-NMR: δ -1.98 (Me-Si), 28.89 ($CH_2$-I), 133.88 ($H_2C=$), 127.96, 129.27, 134.14 (Ar CH groups), 139.23 (Ar quaternary C), 148.13 (olefinic quaternary C). 8: $R_F$(hexane)=0.12. IR(film): 3480 $cm^{-1}$. $^1H$-NMR ($CDCl_3$): δ 7.4-7.75 (m, 5H), 5.05 (d, J=1.0, 1H), 4.75 (d, J=1.0 Hz, 1H), 2.05 (s, 2H), 1.4 (s, 6H), 0.47 (s, 6H). 9: $R_F$(hexane:ether, 7:1)=0.20. IR(film): 3450, 1640, 975 $cm^{-1}$. $^1H$-NMR($CDCl_3$): δ 7.4-7.7 (m, 5H), 5.55-5.9 (m, 2H), 5.15 (m, 1H), 4.8 (m, 1H), 4.4 (d, J=7 Hz, 1H), 2.0 (s, 2H), 1.9 (d, J=6 Hz, 3H), 1.5 (br s, 1H), 0.45 (s, 6H). 10: $R_F$(hexane)=0.49. IR(film): 2250, 900 $cm^{-1}$. $^1H$-NMR($CDCl_3$): δ 7.4-7.8 (m, 5H), 5.1 (m, 1H), 4.9 (m, 1H), 1.95 (br s, 2H), 0.4 (s, 6H). 11: $R_F$(hexane)=0.4. $^1H$-NMR($CDCl_3$): δ 7.3-7.6 (m, 5H), 5.0 (m, 1H), 4.85 (m, 1H), 2.05 (br s, 2H), 1.85 (br s, 3H), 0.4 (s, 6H). 12: $R_F$(hexane:ether, 7:2)=0.2. IR(film):3360, 890 $cm^{-1}$. $^1H$-NMR($CDCl_3$): δ 7.3-7.6 (m, 5H), 4.91 (br s, 1H), 4.68 (br s, 1H), 3.84 (br s, 2H), 1.78 (s, 2H), 0.37 (s, 6H). $^{13}C$-NMR: δ -2.90, 22.70, 67.13, 107.75, 127.91, 129.28, 133.65, 147.19.
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