

THE SILYL-CUPRATION AND STANNYL-CUPRATION OF ALLENES

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Summary—The stoichiometric silyl-cupration of allene **7**, followed directly by treating the intermediate cuprate with a proton, with a range of carbon electrophiles, and with chlorine gives the vinylsilanes **8-13**. Alternatively, when iodine is the electrophile, the product is the vinyl iodide **16**. This can then be metallated and treated with a proton or a range of



carbon electrophiles to give the allylsilanes **18-21**. More-substituted allenes also undergo silyl-cupration followed by protonation, phenylallenes giving vinylsilanes, and alkylallenes giving, on the whole, allylsilanes. Stoichiometric stannyl-cupration of allenes takes place, with similar but less reliable regiocontrol to that of the corresponding silyl-cupration.

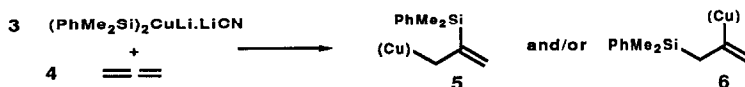
INTRODUCTION

Metallo-metallation of an unactivated C=C π bond in the general sense **1** \rightarrow **2** is a powerful and synthetically useful new reaction, because it creates two adjacent and usually differentiated



nucleophilic carbon atoms, with one metal a transition metal and the other a main group metal.¹⁻⁵ Most known examples of this type of reaction are metallo-cuprations of acetylenes, either stoichiometric¹ or catalytic² in copper, and the products **2** are, twice over, vinyl metal species.

Recently Oshima and his co-workers reported⁴ the addition of silicon-magnesium, silicon-aluminium, and silicon-zinc bonds to unactivated allenes, catalysed by copper(I) or palladium, and we reported⁵ the stoichiometric silyl-cupration of unactivated allenes. In our work,

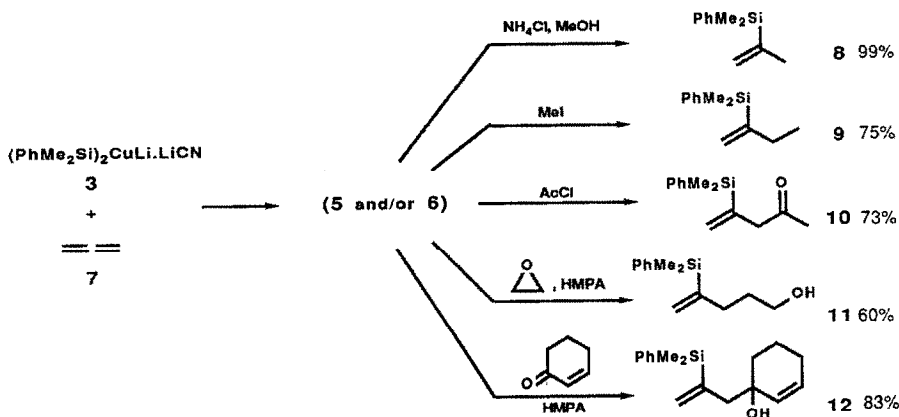


using our silyl-cuprate reagent **3**,⁶ the products were either allyl-copper species (and vinylsilanes) **5** (or a π -allyl equivalent) or vinyl-copper species (and allylsilanes) **6**, depending upon the degree of substitution of the allene **4**. In this paper, we provide details of the work published in

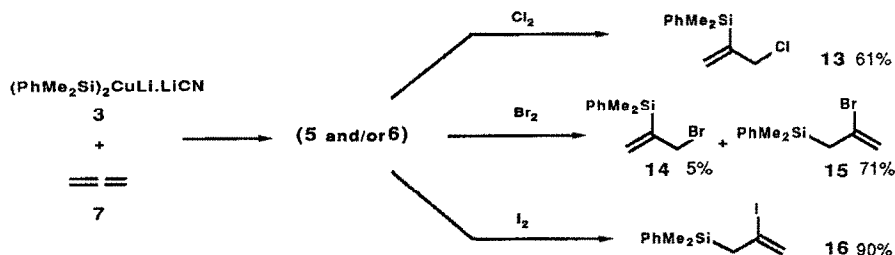
preliminary form,⁵ discuss the factors governing the regiochemistry of the silyl-cupration, with some new experiments reflecting on that problem, and we report for the first time the stoichiometric stannyl-cupration of allenes. The corresponding carbocupration of allenes is not known, except when activating substituents are present, either carbonyl substituents⁷ or alkoxy substituents.⁸

SILYL-CUPRATION OF ALLENE ITSELF

The silyl-cuprate reagent (with the stoichiometric composition 3, and formally a higher-order cuprate) reacted with allene 7 at dry-ice acetone temperatures and the product, indefinitely formulated as 5 and/or 6, was quenched at this temperature with a variety of electrophiles,



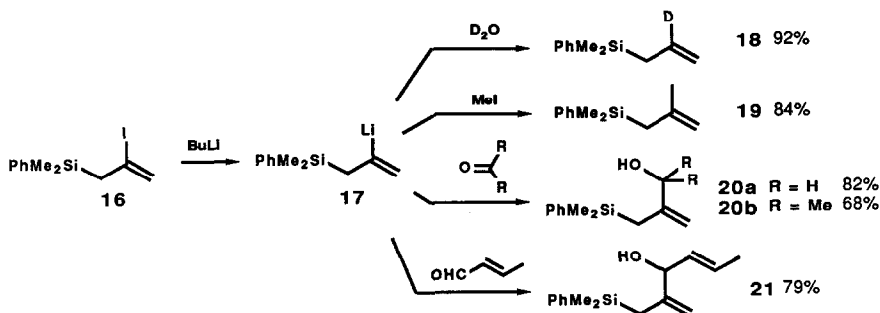
giving, in each case, with the striking exception of bromine and iodine, the vinylsilanes 8-13. Bromine gave a mixture of the vinylsilane 14 and the allylsilane 15, and iodine gave only the allylsilane 16. There was no ambiguity about the structure of this product. The chemical shift of the methylene protons, a singlet at δ 2.55, was appropriate for the allylsilane structure.



Furthermore, treatment of the chloride 13 with sodium iodide gave the clearly distinguishable regioisomer, 2-dimethyl(phenyl)silylallyl iodide, the methylene protons of which appeared as a singlet at δ 3.5, appropriate for the allyl iodide structure.

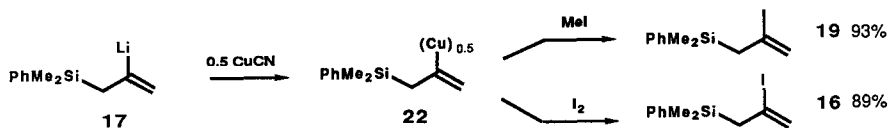
The most obvious explanation for this change in regioselectivity is that the silyl-cupration is a rapid and reversible reaction, with the allyl-copper or cuprate species 5 being more abundant or more reactive than its isomer 6 with most electrophiles. Reversibility in stoichiometric metallo-metallations is common; some reactions, for example, can only be brought to completion by including a proton source, with a consequent severe limitation in the range of electrophiles. In addition, we have evidence of the reversibility of our own reaction in the silyl-cupration of trimethylallene, see later.

Whatever, the explanation, the overall regiochemistry in the silyl-cupration of allene itself is easily controlled in either sense, for a wide range of electrophiles. The direct reaction, as described above, gives an intermediate that is, effectively, the allyl-copper (or cuprate) **5** and hence gives the vinylsilanes **8-13**, whereas the formation of the iodide **16** allows us indirectly to

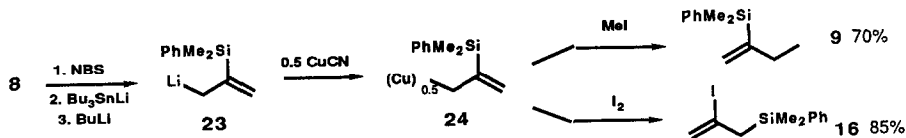


prepare the corresponding vinyl-lithium reagent **17**, which reacts with electrophiles, in the alternative regiochemical sense, to give the allylsilanes **18-21**. In the absence of copper salts, the synthon **17** is evidently regiochemically stable.

However, it has also proved to be regiochemically stable in the presence of copper(I) salts, which indicates that the reversibility of the silyl-cupration may not be the explanation of the curious change of regioselectivity when iodine is the electrophile. When we treated the vinyl-lithium **17** with one half an equivalent of copper(I) cyanide (or iodide), to make the cuprate **22**, and treated this with methyl iodide or iodine, the products were unexceptionally the



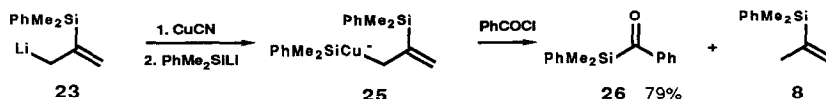
allylsilanes **19** and **16**, respectively. In contrast, the regioisomeric cuprate **24**, which we prepared from the allyl bromide **14** by way of the allyl-lithium reagent **23**, showed the same pattern of reactivity as the original mixture (**5** and/or **6**), giving the vinylsilane **9** with methyl iodide and the



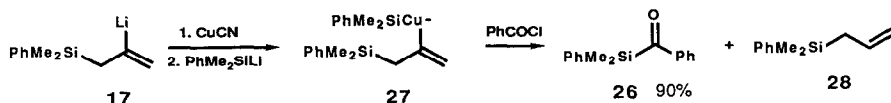
allylsilane **16** with iodine. The reconstituted cuprates **22** and **24** are evidently not in rapid equilibrium. Two possibilities remain: we have not, in reconstituting the cuprate **22**, obtained the same species as that produced in the original reaction mixture, or the cuprate **24**, is essentially the same as that produced in the original reaction mixture but anomalously reacts with iodine to give **16**.

Some indication of the difficulty in characterising and identifying the intermediates is revealed by the following consideration. One might expect that the cuprate **5** in the original reaction mixture would be the mixed higher-order cuprate **25**, in which the copper would have one carbon ligand, one silyl ligand (left over from the use of a disilyl-cuprate **3**), and one cyano ligand at least. We prepared this cuprate by mixing the lithium reagent **23** with one equivalent of copper(I) cyanide and one equivalent of dimethyl(phenyl)silyl-lithium, and found that it transferred the silyl

group to benzoyl chloride giving the benzoylsilane **26** and, after aqueous workup, the vinylsilane **8**. This is exactly what we expected by analogy with work we had done earlier⁹ with mixed



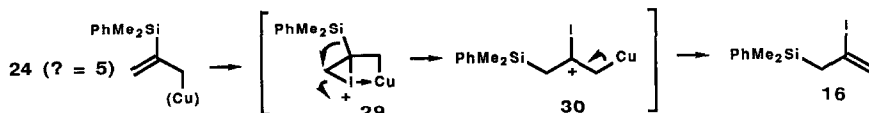
alkyl-silyl higher-order cuprates, where we found that the silyl group was transferred to electrophiles rather than the carbon group. The formation of the products **8-13**, in which the carbon group has been transferred to the electrophile, are therefore anomalous. Similarly, we prepared the mixed cuprate **27** from the lithium reagent **17**. This cuprate ought to



resemble the product **5** from the silyl-cupration of allene, but it too transferred the silyl group to benzoyl chloride and the products were the benzoylsilane **26** and the allylsilane **28**. These cuprates are evidently not the species, **5** and/or **6**, present after the silyl-cupration of allene, nor are they interconverting.

Thus we are not able yet to define precisely the nature of the cuprate produced in the silyl-cupration, and we cannot be dogmatic that the cuprates, **5** and/or **6**, are not rapidly interconverting. If they are interconverting, we still have to explain why iodine (and bromine to a large extent) reacts with the isomer **6**, where everything else reacts with the isomer **5** (or a π -allyl equivalent).

The second possibility, that the iodination is simply an anomalous reaction of the allyl-copper or cuprate **24** (which may or may not be the same as **5**), is also difficult to accept. However, iodine is simultaneously a soft electrophile and nucleophile, and it may attack the allyl-copper or cuprate to give an intermediate, loosely drawn as **29**, in which the coordination of the iodine to the copper may explain why this electrophile is anomalous. Rearrangement of the silyl group (**29** arrows) is



not stereoelectronically well set up, but might be feasible in a less concerted version than the arrows imply; loss of the copper from the intermediate **30** is then unexceptional.

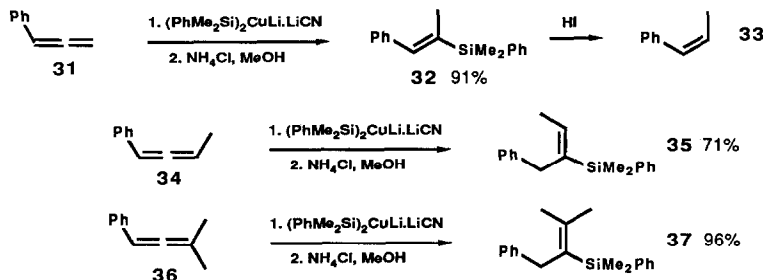
The regiochemistry in the direct reaction forming the vinylsilane products of the type **8-11** is the same as that found by Oshima and his co-workers⁴ using catalytic silyl-metallation conditions. In their work, iodine was not used as an electrophile. Trimethylsilyl-lithium¹⁰ is less easily prepared than dimethyl(phenyl)silyl-lithium,¹¹ but the derived cuprate gives the same result as with dimethyl(phenyl)silyl, although we only looked at protonation of the intermediate: the product was 2-trimethylsilyl-1-propene. In contrast *t*-butyldiphenylsilyl-lithium gives a cuprate showing opposite regioselectivity: with all electrophiles tried so far the products are allylsilanes.¹²

SILYL-CUPRATION OF SUBSTITUTED ALLENES

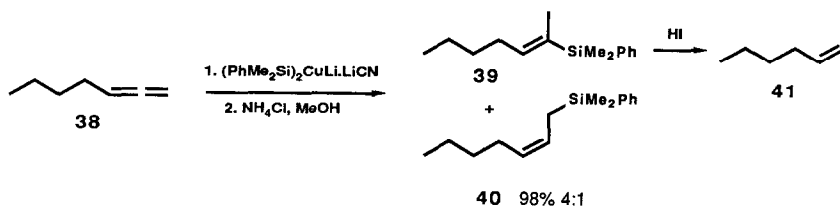
With substituted allenes, we have not yet examined every electrophile in order to determine the regiochemistry, but the following results indicate the trends to be expected. With unsymmetrical allenes there is a large number of possible products: two regioisomers in the silyl-cupration reaction, two allylic regioisomers from each allyl-cuprate intermediate, two allylsilane isomers from

each vinyl-cuprate intermediate, and geometrical (Z or E) isomers of several of these regioisomers. It is remarkable that the reactions we actually observe are comparatively selective among all these products.

Phenylallenes—The phenylallenes **31**, **34**, and **36** reacted with the silyl-cuprate reagent, followed by methanolic ammonium chloride, to give the vinylsilanes **32**, **35**, and **37**. We proved that the vinylsilane **32** had the E geometry by stereospecific protodesilylation to the Z-alkene **33**. These results are reasonable in giving phenyl-stabilised allyl-cuprates by attack on the allene anti to the phenyl group, and protodecupration to give, on the whole, the more stable alkene, but more examples are needed to confirm this simple picture.

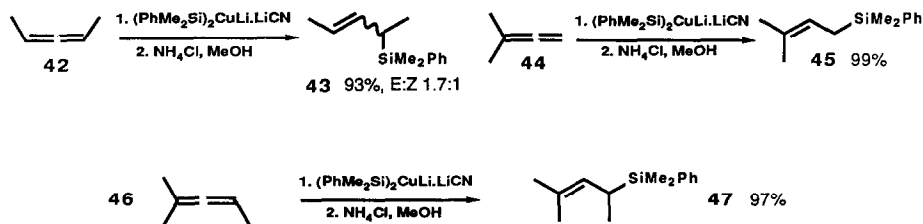


Alkylallenes—The monosubstituted allene **38** gave a mixture of the regioisomers **39** and **40** in a ratio of 4:1, respectively, on silyl-cupration followed by protodecupration. The regiochemical change giving some of the allylsilane is reasonable if we accept that alkyl groups destabilise the



allyl-cuprate regioisomer, and the stereochemistry, proved by protodesilylation to **41**, is reasonable in that the silyl-cuprate has attacked anti to the butyl group in both regioisomers.

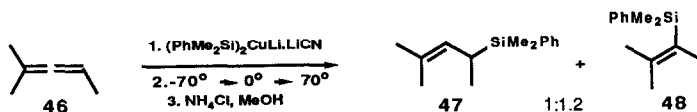
1,3-Dimethylallene (**42**), 1,1-dimethylallene (**44**), and 1,1,3-trimethylallene (**46**) all gave a single regioisomer, now favouring entirely the production of the allylsilanes **43**, **45**, and **47**, respectively. The only anomaly here is the higher proportion of the E isomer of **43** over the Z, since this



corresponds to attack of the silyl-cuprate reagent syn to a methyl group. It appears that in these three reactions the regiochemistry is cleanly that corresponding to the formation of the regioisomer **6**, having the vinyl-copper or cuprate and allylsilane structure.

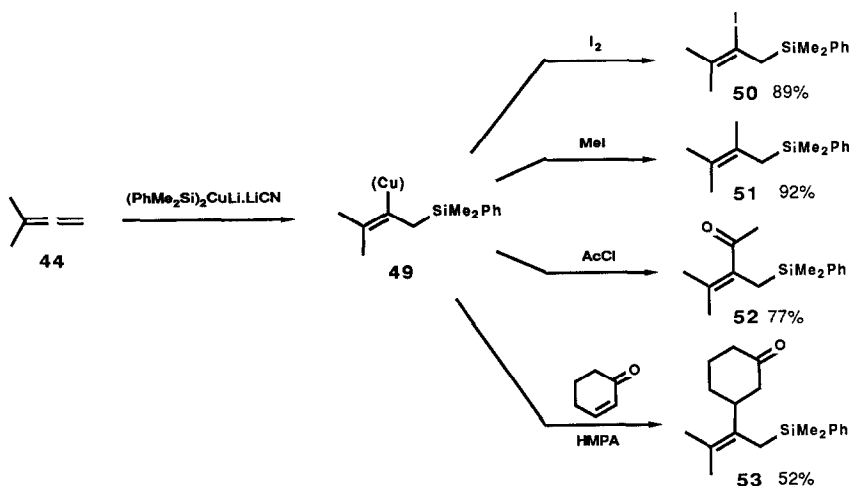
Using the allene **44**, we confirmed that the trimethylsilyl-cuprate reacts with the same regiochemistry as the phenyldimethylsilyl-cuprate: the product after protodecupration was the known 3,3-dimethylallyltrimethylsilane. The reversibility of the silyl-cupration step was evident

from one observation on 1,1,3-trimethylallene (46). The result described above is that observed when the silyl-cupration was followed immediately by protonation, the whole mixture being maintained at dry-ice acetone temperatures. Instead, when we warmed the intermediate to 0°C for one hour before quenching it at dry ice-acetone temperatures, we obtained two products: the



allylsilane 47, as before, and the vinylsilane 48 in nearly equal amounts. This reaction not only demonstrates the reversibility of silyl-cupration, admittedly in the case most likely to be easily reversible, but it also indicates that the protocol, and the care with which the reaction is carried out, may influence the outcome.

We treated the presumed intermediate 49 produced from 1,1-dimethylallene (44) with other electrophiles, including iodine, and cleanly obtained the derived allylsilanes 50-53.



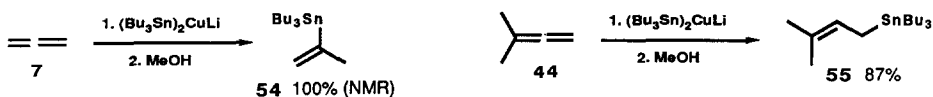
The regiochemistry in all these reactions is similar to that found by Oshima and his co-workers⁴ in the palladium-catalysed silyl-alumination and silyl-zincation of allenes: a monosubstituted allene gave mixtures of allylsilanes and vinylsilanes, and a 1,3-disubstituted allene gave largely the allylsilane regioisomer. In their work, they were able to control the regioisomer to some extent by changing to copper(I)-catalysed silyl-magnesiation, in which both a mono-substituted allene and a 1,3-disubstituted allene gave largely the corresponding vinylsilanes.

In summary silyl-cupration of allenes, followed by direct or indirect electrophilic attack, gives rise to a wide variety of allylsilanes and vinylsilanes, functionalised or not depending upon the nature of the electrophile. Some of these products are of a type already used in synthesis, for example the trimethylsilyl analogues of 20a and 20b,^{14,15} for which the present method is an attractively simple synthesis, and the others have similarly considerable potential in allylsilane and vinylsilane chemistry.¹⁶ Furthermore, the phenyldimethylsilyl group can be converted into a hydroxy group in a simple one-pot procedure.¹⁷

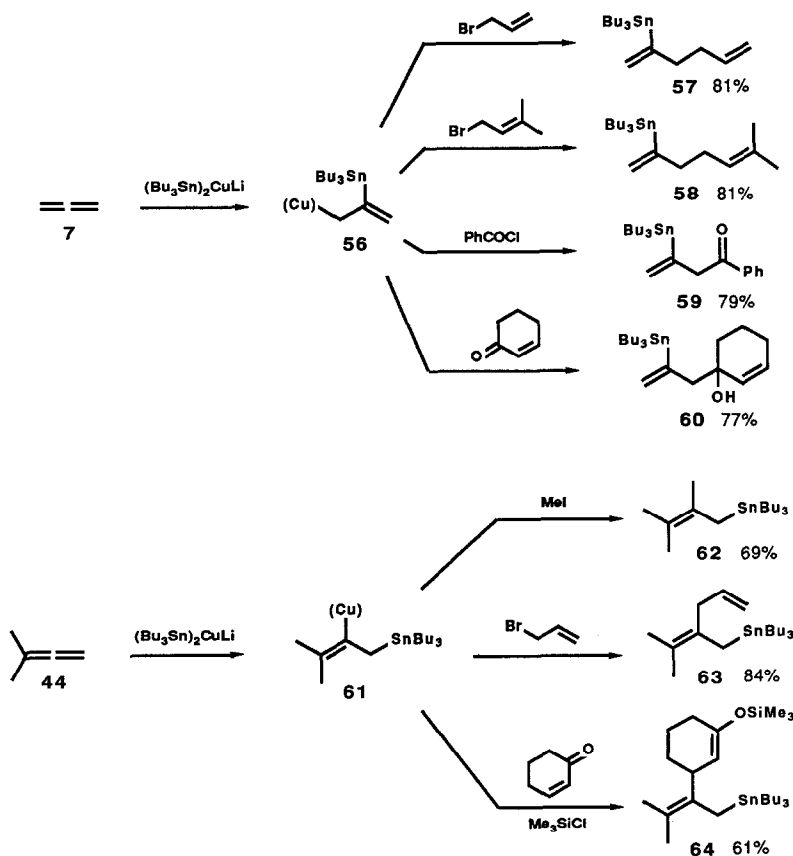
The outstanding problem in this work is to determine more precisely the nature of the copper-containing intermediates. This problem is common both to this work and to our work on the silyl-cupration of acetylenes,¹ where we also observe carbon electrophiles reacting with an intermediate with carbon-carbon bond formation, when silicon-carbon bond formation would have been expected from the mixed cuprates that we have always written as the presumed intermediates.

STANNYL-CUPRATION OF ALLENES

We have also investigated briefly the corresponding stannyl-cupration of the allenes **7** and **44**. Although we had no identifiable products using a trimethylstannyl-cuprate reagent, we find that both allenes react with a cuprate reagent prepared from two equivalents of tributyltin-lithium and one of the copper(I) bromide-dimethylsulphide complex (Piers' reagent, and formally a lower-order cuprate), and the products of protodecupration are the vinylstannane **54** and the allylstannane **55**,

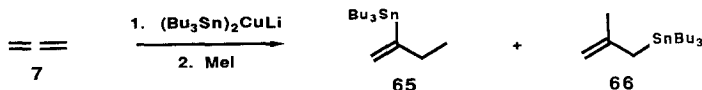


respectively. The regioselectivity is therefore the same as that for the corresponding silyl-cuprations. A number of carbon electrophiles also combine with the presumed copper (or cuprate) intermediates, **56** and **61**, giving the vinylstannanes **57-60** from **56**, and the allylstannanes **62-64**



from **61**. However, the reaction of the presumed copper intermediate **56**, derived from allene itself, with methyl iodide revealed that this seemingly orderly pattern may not be the whole story. In this case, there were two products, the vinylstannane **65** and the allylstannane **66**, which were clearly visible from characteristic peaks in the $^1\text{H-NMR}$ spectrum. Since the corresponding by-products in the other reactions illustrated may not have given characteristic peaks in the $^1\text{H-NMR}$ spectra of the reaction products, it may well be that the reactions are not as clean as they seem. The spectra are, in any case, heavily dominated by the signals from the three butyl groups.

Furthermore, we repeated the last reaction many times and found that the products **65** and **66** were not formed reproducibly in the same ratio every time, the extremes being from 80:20 to 15:85. In



spite of much work, we are not yet able to identify either the cause or the cure for this problem. The results we report here are therefore preliminary in nature; all that is certain is that the stannyl-cupration of allenes is an easy reaction with much potential.

EXPERIMENTAL

We bought the allenes **7** and **44**. The allenes **31** (54%), **34** (83%), **38** (40%), **42** (41%), and **46** (60%) were prepared by the method of Crabbé.¹⁸

1-Phenyl-3-methyl-1,2-butadiene (36).—Following Crabbé,¹⁸ 2-methyl-3-butyn-2-ol acetate (6.3 g) in ether (20 ml) was added dropwise to phenyl-lithium (83 ml of a 1.2M solution in Et₂O) and the mixture kept under nitrogen for 2 h. An aqueous work-up gave the allene (6.1 g, 84%), b.p. 106–108 °C/17 mmHg, IR(film) 1940 and 1589 cm⁻¹, ¹H-NMR δ(CDCl₃) 7.25–7.45 (5H, m, Ph), 6.08 (1H, septet, *J*, 3 Hz, C=CH), and 1.9 (6H, d, *J* 3 Hz, Me)(Found: \bar{M}^+ , 144.0952. C₁₁H₁₂ requires \bar{M} , 144.0939), m/z 144 (61%, \bar{M}^+) and 129 (100, \bar{M} - Me).

General Procedure for the Silyl-Cupration of Allenes.—Typically, the allene (4 mmol) in THF (3 ml) was added dropwise to the dimethyl(phenyl)silyl-cuprate reagent⁶ or the dibutylmethylsilyl-cuprate⁹ (4.4 mmol) cooled with a dry-ice/acetone bath, and the mixture stirred under nitrogen for 1 h. Yields are based on the allene.

The Preparation of the Lithium Reagent 17.—*n*-Butyl-lithium (2.7 ml of a 1.6M solution in hexane) was added dropwise to the vinyl iodide **16** (4 mmol) in THF (5 ml) at dry-ice/acetone temperatures, and the mixture stirred under nitrogen for 30 min.

The Preparation of the Cuprate Reagent 22.—The lithium reagent **17** (2 mmol) and copper(I) cyanide (1 mmol) were stirred together at 0 °C for 30 min.

The Preparation of the Cuprate Reagent 24.—The bromide **14** (1.28 g, 5 mmol) in THF (6 ml) was added slowly to a solution of tributylstannyl-lithium¹⁹ (2.4 ml of a 2.08M solution in THF) at 0 °C and the mixture stirred for 1 h. After 1 h at room temperature it was worked up to give the allylstannane (72%) IR(film) 1600, 1260, and 1135 cm⁻¹, ¹H-NMR δ(CDCl₃) 7.4–7.1 (5H, m), 5.4 (1H, m), 5.15 (1H, d, *J*, 1.5 Hz), 1.85 (2H, br s), and 1.2–0.8 (27H, m). *n*-Butyl-lithium (1.25 ml of a 1.6M solution in hexane) was added dropwise to the allylstannane (2 mmol) in ether (3 ml) at 0 °C and the mixture stirred for 20 min. THF (5 ml) and copper(I) cyanide (1 mmol) were added and the black solution stirred for 30 min.

The Preparation of the Cuprate Reagent 25.—The lithium reagent **23** (2 mmol)(prepared as described above in the preparation of the cuprate **24** and diluted with THF) was stirred with copper(I) cyanide (2 mmol) at 0 °C for 15 min, the silyl-lithium reagent (2 mmol) was then added and the mixture stirred for a further 35 min.

The Preparation of the Cuprate Reagent 27.—The lithium reagent **17** (2 mmol) and copper(I) cyanide (2 mmol) were stirred together at 0 °C for 15 min, the silyl-lithium reagent (2 mmol) was then added and the mixture stirred for a further 30 min.

General Procedure for the Stannyl-Cupration of Allenes.—Following Piers and Chong,¹ the copper bromide:dimethylsulphide complex²⁰ (175 mg, 0.85 mmol) in THF:dimethylsulphide (2ml, 1:1) was added dropwise over 3 min to a stirred solution of tributyltin-lithium (1.73 mmol, prepared from hexabutylstannane) in THF (10 ml) at dry-ice/acetone temperatures, and the orange solution stirred for 15 min. Excess of the allene (2 mmol) was added, and the mixture stirred for 15 min. Yields are based on the stannyl-cuprate reagent, on the assumption that one of the stannyl groups is available.

Protonation of the Organometallic Intermediates.—Methanol (2 ml) saturated with ammonium chloride was added to the still cold solution following the silyl-cupration, the stannyl-cupration, or the halogen-metal exchange, as appropriate; the mixture was allowed to warm to 0 °C and stirred for 10 min. An aqueous workup using ether, drying with magnesium sulphate, and chromatography (SiO₂, hexane) gave the following compounds: 2-Dimethyl(phenyl)silylpropene (**8**)(99%) IR(film) 1609, 1253, and 1124 cm⁻¹, ¹H-NMR δ(CDCl₃) 7.75–7.4 (5H, m), 5.75 (1H, m, C=CH *trans* to Si), 5.42 (1H, m, C=CH *cis* to Si), 1.9 (3H, d, *J* 1.3 Hz), and 0.44 (6H, s)(Found: \bar{M}^+ , 176.1025.

$C_{11}H_{16}Si$ requires M , 176.1022), m/z 176 (21%, M^+), 161 (71), and 135 (100). 2-Trimethylsilylpropene (91%) IR(film) 1630, 1240, and 910 cm^{-1} , 1H -NMR δ ($CDCl_3$) 5.53 (1H, m), 5.16 (1H, m), 1.8 (3H, d, J 1.3 Hz), and 0.13 (9H, s)(Found: M^+ , 99.0622. $C_8H_{14}Si$ - Me requires M , 99.0630), m/z 99 (30%, M^+ - Me) and 73 (100). 2-Deuterio-3-dimethyl(phenyl)silylpropene (18)(92%)(quenching with deuterium oxide in place of the methanol, and omitting the ammonia)(Found: C, 74.2; H, 9.45. $C_{11}H_{15}DSi$ requires C, 74.5; H, 9.65%) IR(film) 2250 and 900 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.8-7.4 (5H, m), 5.1 (1H, m), 4.9 (1H, m), 1.95 (2H, br s), and 0.4 (6H, s). (E)-1-Phenyl-2-dimethyl(phenyl)silylpropene (32)(91%) IR(film) 1609, 1583, 1255, and 1115 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.2 (10H, m), 6.9 (1H, q, J 1.5 Hz), 1.95 (3H, d, J 1.5 Hz), and 0.47 (6H, s)(Found: M^+ , 252.1321. $C_{11}H_{20}Si$ requires M , 252.1334), m/z 252 (60%, M^+), 237 (53), 174 (6), and 135 (100). (E)-1-Phenyl-2-dimethyl(phenyl)silylbut-2-ene (35)(71%) IR(film) 1608, 1592, 1257, and 1125 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.2 (10H, m), 6.2 (1H, q, J 7.5 Hz), 3.57 (2H, s), 1.78 (3H, d, J 7.5 Hz), and 0.41 (6H, s)(Found: M^+ , 266.1471. $C_{13}H_{22}Si$ requires M , 266.1490), m/z 266 (4%, M^+), 188 (5), 173 (5), and 135 (100). 1-Phenyl-2-dimethyl(phenyl)silyl-3-methylbut-2-ene (37)(96%) IR(film) 1610, 1585, 1255, and 1120 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.3 (5H, m), 3.72 (2H, s), 1.94 (6H, s), and 0.41 (6H, s)(Found: M^+ , 280.1662. $C_{13}H_{24}Si$ requires M , 280.1647), m/z 280 (3%, M^+), 265 (9), 202 (66), 187 (50), and 135 (100). (E)-2-Dimethyl(phenyl)silylhept-2-ene (39) and (Z)-1-dimethyl(phenyl)silylhept-2-ene (40)(98%) in a ratio of 4:1; these were separated: 39 Rf (hexane) 0.41, IR(film) 1617, 1255, and 1123 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.4 (5H, m), 5.9 (1H, tq, J 6.5 and 1.5 Hz), 2.2 (2H, br q, J 6.5 Hz), 1.75 (3H, d, J 1.5 Hz), 1.35 (4H, m), 0.97 (3H, t, J 7 Hz), and 0.40 (6H, s)(Found: M^+ , 232.1636. $C_{15}H_{24}Si$ requires M , 232.1648), m/z 232 (16%, M^+), 217 (24), 175 (20), and 135 (100); 40 Rf (hexane) 0.34, IR(film) 1637, 1255, 1125 and 703 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.4 (5H, m), 5.4 (2H, m), 2.0 (2H, br q, J 6.9 Hz), 1.77 (2H, d, J 7.7 Hz), 1.31 (4H, m), 0.92 (3H, t, J 7 Hz), and 0.36 (6H, s)(Found: M^+ , 232.1654), m/z 232 (6%, M^+), 217 (5), and 135 (100). (E)- and (Z)-4-Dimethyl(phenyl)silylpent-2-ene (43)(93%) in a ratio of 3:1 (or 1.7:1 when the mixture was warmed to 0°C before quenching) IR(film) 1642, 1255, 1125, and 990 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.8-7.4 (5H, m), 5.4 (2H, m), 2.19 (dq, J 10 and 7.5 Hz, Z-isomer) and 1.82 (total 1H, quintet, J 7.5 Hz, E-isomer), 1.72 (d, J 6 Hz, E-isomer) and 1.53 (total 3H, d, J 6 Hz, Z-isomer), 1.08 (3H, t, J 7.5 Hz), and 0.33 (6H, s)(Found: M^+ , 204.1349. $C_{13}H_{20}Si$ requires M , 204.1334), m/z 204 (3%, M^+) and 135 (100). 3-Methyl-1-dimethyl(phenyl)silylbut-2-ene (45)(99%) IR(film) 1658, 1258, and 1123 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.8-7.4 (5H, m), 5.28 (1H, br t, J 9 Hz), 1.82 (3H, s), 1.72 (2H, d, J 9 Hz), 1.6 (3H, br s), and 0.34 (6H, s)(Found: M^+ , 204.1331), m/z 204 (14%, M^+) and 135 (100). 3-Methyl-1-trimethylsilylbut-2-ene²¹ (97%) IR(film) 1660 and 1240 cm^{-1} , 1H -NMR δ ($CDCl_3$) 5.18 (1H, br t, J 9 Hz), 1.72 (3H, s), 1.60 (3H, s), 1.55 (2H, d, J 9 Hz), and 0.05 (9H, s)(Found: M^+ , 142.1182. $C_8H_{18}Si$ requires M , 142.1178), m/z 142 (2%, M^+) and 73 (100). 2-Methyl-4-dimethyl(phenyl)silylpent-2-ene (47)(97%) IR(film) 1245, and 1115 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.75-7.35 (5H, m), 5.03 (1H, br d, J 11.5 Hz), 1.82 (3H, s), 2.03 (1H, dq, J 11.5 and 7 Hz), 1.74 (3H, br s), 1.53 (3H, br s), 1.09 (3H, d, J 7 Hz), 0.36 (3H, s), and 0.33 (3H, s)(Found: M^+ , 218.1505. $C_{14}H_{22}Si$ requires M , 218.1490), m/z 218 (12%, M^+), 203 (10), and 135 (100); when the reaction mixture in this case was quenched at 0°C , the allylsilane 47 and the vinylsilane 48 were formed in a ratio of 1:1.2; these were not separated but the vinylsilane was identified by the following extra, or overlapping, signals in the spectra: IR(film) 1610 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.4 (5H, m), 2.26 (2H, q, J 7.5 Hz), 1.87 (3H, s), 1.77 (3H, br s), 1.03 (3H, t, J 7.5 Hz), and 0.49 (6H, s)(Found: M^+ , 218.1496. $C_{14}H_{22}Si$ requires M , 218.1490), m/z 218 (9%, M^+), 203 (3), and 135 (100); the same mixture in the same proportions was obtained when the warming to 0°C was followed by cooling the solution back to dry-ice/acetone temperatures before quenching. 2-Tributylstannylpropene (54)(100%, NMR) IR(film) 1620 cm^{-1} , 1H -NMR δ ($CDCl_3$) 5.68 (1H, dq, J 3 and 1.5 Hz), 5.08 (1H, dq), J 3 and 1.5 Hz), 1.96 (3H, t, J 1.5 Hz), and 1.6-0.7 (27H, m), m/z 331 (3%, M^+ - H), 291 (36), and 275 (100). 2-Methyl-4-tributylstannylbut-2-ene²² (55)(87%) IR(film) 3000 - 2900 cm^{-1} , 1H -NMR δ ($CDCl_3$) 5.29 (1H, br t, J 9 Hz), 1.68 (3H, s), 1.57 (3H, s), and 2.3-0.7 (29H, m), m/z 360 (7%, M^+), 291 and (100).

Methylation of the Cuprate and Lithium Intermediates.—Methyl iodide (3 mmol) was added dropwise to the silyl-cupration mixture (2 mmol)(or one of the other cuprate or lithium intermediates described in the text) and stirred at dry-ice/acetone temperatures for 1 h and then at 0°C for 1 h. An aqueous workup using ether, and chromatography gave the following compounds: 2-Dimethyl(phenyl)silylbut-1-ene (9)(75% from 5, 70% from 24) IR(film) 1609, 1253, and 1124 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.4 (5H, m), 5.79 (1H, m), 5.46 (1H, m), 2.18 (2H, br q, J 7 Hz), 1.0 (3H, t, J 7 Hz), and 0.42 (6H, s)(Found: M^+ , 190.1184. $C_{12}H_{18}Si$ requires M , 190.1178), m/z 190 (19%, M^+), 175 (31), and 135 (100). 2-Methyl-3-dimethyl(phenyl)silylpropene (19)(84% from 17, 93% from 22)(Found: C, 75.6; H, 9.4. $C_{12}H_{18}Si$ requires C, 75.7; H, 9.5%) 1H -NMR δ ($CDCl_3$) 7.6-7.3 (5H, m), 5.0 (1H, m), 4.85 (1H, m), 2.05 (2H, br s), 1.85 (3H, br s), and 0.4 (6H, s). 1-Dimethyl(phenyl)silyl-2,3-dimethylbut-2-ene (51)(92%) IR(film) 1260 and 1120 cm^{-1} , 1H -NMR δ ($CDCl_3$) 7.7-7.4 (5H, m), 1.8 (2H, m), 1.67 (3H, s), 1.6 (3H, s), 1.55 (3H, br s), and 0.32 (6H, s)(Found: M^+ , 218.1490. $C_{14}H_{22}Si$ requires M , 218.1490), m/z 218 (9%, M^+) and 135 (100). 2,3-Dimethyl-4-tributylstannylbut-2-ene (62)(69%) IR(film) 1640 cm^{-1} , 1H -NMR δ ($CDCl_3$) 1.72 (2H, s), 1.64 (3H, s), 1.61 (6H, s), 1.6-1.2 (12H, m), 0.87 (9H, t, J 7 Hz), and 0.82 (6H, t, J 8 Hz), m/z 374 (9%, M^+), 291 (88), and 269 (100). A mixture of 2-tributylstannylbutene (65) IR(film) 1620 cm^{-1} , 1H -NMR δ ($CDCl_3$) 5.67 (1H, dt, J 2.8 and 1.5 Hz), 5.08 (1H, dt, J 2.8 and 1.3 Hz), 2.26 (2H, ddq, J 1.3, 1.5, and 7.4 Hz), and 1.6-0.7 (30H, m), m/z 346 (1%, M^+), 291 (95), and 289 (100), and the vinylsilane²³ (66) 1H -NMR δ ($CDCl_3$) 4.48 (1H, br s), 4.44 (1H, br s), 1.79 (2H, s), 1.71 (3H, s), and 1.6-0.6 (27H, m); typically the ratio was 4:1, but this was not reproducible, as explained in the text. The highest proportion of 66 was obtained when we used freshly opened Aldrich Gold Label copper(I) bromide to prepare the dimethylsulphide complex.

Acylation of the Intermediate.—Acetyl chloride or benzoyl chloride (2.25 mmol) was added to the silyl-cupration mixture (1.5 mmol)(or the stannyl-cupration mixture or the cuprates 25 or 27) as in the methylation reactions above to give the following compounds: 4-Dimethyl(phenyl)silylpent-

4-ene-2-one (10) (73%) IR(film) 1705, 1260, and 1120 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.3 (5H, m), 5.83 (1H, br d, J 1.5 Hz), 5.7 (1H, d, J 1.5 Hz), 3.23 (2H, br s), 2.05 (3H, s), and 0.46 (6H, s)(Found: M^+ , 203.0887. $\text{C}_{13}\text{H}_{18}\text{OSi}$ requires $M - \text{Me}$, 203.0892), m/z 203 (100%, $M^+ - \text{Me}$), 141 (62), and 135 (41). **Benzoyldimethyl(phenyl)silane (26)** (79% from **25** and 90% from **27**) m.p. 55-57 $^\circ\text{C}$ (from hexane)(lit.²⁴ 54-55 $^\circ\text{C}$). **3-Dimethyl(phenyl)silylprop-2-ene-2-one (52)** (77%) IR(film) 1690, 1620, 1245, and 1110 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.3 (5H, m), 2.15 (3H, s), 2.0 (2H, s), 1.81 (3H, s), 1.57 (3H, s), and 0.31 (6H, s)(Found: M^+ , 231.1213. $\text{C}_{15}\text{H}_{22}\text{OSi}$ requires $M - \text{Me}$, 231.1205), m/z 231 (25%, $M^+ - \text{Me}$) and 135 (100). **1-Phenyl-3-tributylstannylbut-2-en-1-one (59)** (79%) IR(film) 1680, 1600, 1580, and 930 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.96 (2H, d, J 7 Hz), 7.52 (1H, t, J 7 Hz), 7.45 (2H, t, J 7 Hz), 5.82 (1H, br s), 5.36 (1H, br s), 3.93 (2H, br s), and 0.7 (27H, m), m/z 435 (1%, M^+), 379 (100, 291 (6), and 105 (8).

4-Dimethyl(phenyl)silylprop-4-ene-1-ol (11).—Hexamethylphosphoric triamide (HMPA)(3 mmol) in THF (1 ml) was added to the silyl-cupration mixture (3 mmol) at dry-ice/acetone temperatures, kept for 5 min and then ethylene oxide (6 mmol) was added; after 30 min the mixture was warmed to 0 $^\circ\text{C}$ and kept for 8 h before the usual workup, which gave the **vinylsilane (60)**(Found: C, 70.6; H, 9.0. $\text{C}_{15}\text{H}_{20}\text{OSi}$ requires C, 70.8; H, 9.15%) IR(film) 3360, 1250, and 1110 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.6-7.2 (5H, m), 5.65 (1H, m), 5.4 (1H, m), 3.45 (2H, t, J 7 Hz), 2.1 (2H, br t, J 7.5 Hz), 1.95 (1H, br s, OH), 1.55 (2H, br q, J 7 Hz), and 0.4 (6H, s).

Reactions with Cyclohexenone.—HMPA (0.5 ml) in THF (1 ml) was added to the cuprate reagent (3 mmol) at dry-ice/acetone temperatures, and cyclohexenone (4.5 mmol) in THF (1 ml) added after 10 min. The mixture was kept for 1 h, allowed to warm to 0 $^\circ\text{C}$ and stirred for 1 h. Aqueous workup and chromatography (SiO_2 , Et_2O -hexane) gave the following compounds: **1-[2-Dimethyl(phenyl)silylprop-2-en-1-yl]cyclohex-2-en-1-ol (12)** (83%) IR(film) 3575, 3450, 1640, 1245, 1110, and 900 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.3 (5H, m), 5.9-5.45 (4H, m), 2.41 (2H, s), 1.91 (2H, m), 1.56 (4H, m), 1.35 (1H, s, OH), and 0.4 (6H, s)(Found: M^+ , 272.1577. $\text{C}_{17}\text{H}_{26}\text{OSi}$ requires M , 272.1596), m/z 272 (2%, M^+), 257 (5), 254 (2), 137 (15), 135 (37), and 97 (100). The regiochemistry of this reaction is normal for allyl-cuprates.²⁵ **3-[3-Methyl-1-dimethyl(phenyl)silylbut-2-en-2-yl]cyclohexanone (53)** (52%) IR(film) 1710, 1260, and 1125 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.3 (5H, m), 2.8 (1H, m), 1.85-2.2 (4H, m), 1.73 (2H, s), 1.64 (3H, s), 1.52 (3H, s), 1.7-1.4 (4H, m), and 0.3 (6H, s)(Found: M^+ , 300.1922. $\text{C}_{19}\text{H}_{28}\text{OSi}$ requires M , 300.1909), m/z 300 (5%, M^+), 285 (7), 257 (10), 222 (10), and 135 (100). **1-[2-Tributylstannylprop-2-enyl]cyclohex-2-en-1-ol (60)** (77%) IR(film) 3600, 3400, 1640, 1245, 1110, and 930 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 5.8-5.7 (2H, m), 5.6 (1H, d, J 6 Hz), 5.32 (1H, d, J 3 Hz), 2.46 (2H, s), and 2.4-2.0 and 1.7-0.8 (34H, m), m/z 371 (11%, $M^+ - \text{Bu}$), 353 (100), and 291 (14). The regiochemistry of this reaction is normal for allyl-cuprates.²⁷ **3-[3-Methyl-1-tributylstannylbut-2-en-2-yl]cyclohexanone (52)** IR(film) 1710 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 1.72 (2H, s), 1.64 (3H, s), 1.61 (6H, s), 1.6-1.2 (12H, m), 0.87 (9H, t, J 7 Hz), and 0.82 (6H, t, J 8 Hz), m/z 374 (4%, M^+), 291 (88), and 269 (100). When trimethylsilyl chloride was added before the cyclohexenone,²⁶ workup and flash chromatography (SiO_2 , light petroleum) gave the **silyl enol ether (65)** of this ketone in better yield (61%) IR(film) 1640 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 5.0 (1H, d, J 5 Hz), 2.4-1.7 (42H, m), and 0.16 (9H, s), m/z 471 (0.1%, $M^+ - \text{Bu}$), 331 (100), and 291 (8).

Halogenation of the Silyl-Cupration Products.—Chlorine (3.6 mmol for 3 mmol of cuprate) from a balloon, bromine (2 mmol for 2 mmol) from a syringe, or iodine (1.5 mmol for 1 mmol) in two portions was added to the cuprates at dry-ice/acetone temperatures, kept at this temperature for 1 h, allowed to warm to 0 $^\circ\text{C}$, and kept for 1 h. Workup and chromatography (SiO_2 , pentane, or hexane) gave the following compounds: **3-Chloro-2-dimethyl(phenyl)silylpropene (13)** (61%) (Found: C, 62.9; H, 7.3. $\text{C}_{11}\text{H}_{15}\text{ClSi}$ requires C, 62.7; H, 7.2%), $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.4 (5H, m), 5.6 (1H, d, J 1 Hz), 5.5 (1H, d, J 1 Hz), 4.35 (2H, s), and 0.45 (6H, s), $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 145.45, 138.89, 134.03, 129.35, 128.08, 130.07, 49.13, and -2.72. **3-Bromo-2-dimethyl(phenyl)silylpropene (14)** (5%), Rf(hexane) 0.3, identified by its $^1\text{H-NMR}$ signals (see below) and **2-Bromo-3-dimethyl(phenyl)silylpropene (15)** (71%), Rf(hexane) 0.33 (Found: C, 51.9; H, 6.1. $\text{C}_{11}\text{H}_{15}\text{BrSi}$ requires C, 51.7; H, 5.9%), IR(film) 1605, 1255, and 1125 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.6-7.2 (5H, m), 5.2 (2H, br s), 2.25 (2H, s), and 0.3 (6H, s), $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 137.71, 133.61, 130.34, 129.26, 127.81, 114.81, 32.65, and -3.03. **2-Iodo-3-dimethyl(phenyl)silylpropene (16)** (90% from **5/6**, 89% from **22**, and 85% from **24**)(Found: C, 43.8; H, 5.1. $\text{C}_{11}\text{H}_{15}\text{ISi}$ requires C, 43.7; H, 5.0%), $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.4 (5H, m), 5.72 (1H, d, J 1.2 Hz), 5.59 (1H, d, J 1.2 Hz), 2.55 (2H, s), and 0.5 (6H, s), $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 138.98, 133.80, 129.08, 127.87, 127.27, 104.65, 31.09, and -2.88 (Found: M^+ , 301.9968. $\text{C}_{11}\text{H}_{15}\text{ISi}$ requires M , 301.9987), m/z 302 (3%, M^+), 175 (10), and 135 (100). **2-Iodo-3-methyl-1-dimethyl(phenyl)silylbut-2-ene (50)** (89%) IR(film) 1610, 1257, and 1120 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.35 (5H, m), 2.65 (2H, s), 1.95 (3H, s), 1.61 (3H, s), and 0.47 (6H, s)(Found: M^+ , 330.0294. $\text{C}_{13}\text{H}_{19}\text{ISi}$ requires M , 330.0301), m/z 330 (4%, M^+), 203 (6), and 135 (100).

3-Bromo-2-dimethyl(phenyl)silylpropene (14).—The vinylsilane **8** (1.5 g, 8.5 mmol) and *N*-bromosuccinimide (1.06 g, 6 mmol) were refluxed in carbon tetrachloride (15 ml) for 12 h with a catalytic quantity of benzoyl peroxide. Filtration, evaporation, and chromatography (SiO_2 , hexane) gave the **bromide (14)** (1 g, 66%)(Found: C, 51.8; H, 6.1. $\text{C}_{11}\text{H}_{15}\text{BrSi}$ requires C, 51.8; H, 5.9%) IR(film) 1610, 1250, and 1120 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.6-7.2 (5H, m), 6.05 (1H, m), 5.65 (1H, m), 4.0 (2H, br s), and 0.45 (6H, s), $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 145.92, 136.88, 133.99, 131.05, 129.42, 127.98, 37.24, and -2.53.

3-Iodo-2-dimethyl(phenyl)silylpropene.—The chloride **13** (261 mg, 1.24 mmol) and sodium iodide (281 mg, 1.86 mmol) were refluxed in *n*-butanone (3 ml) for 4 h. An aqueous workup using ether gave the **allyl iodide (327 mg, 87%)(Found: C, 43.8; H, 5.1. $\text{C}_{11}\text{H}_{15}\text{ISi}$ requires C, 43.7; H, 5.0%), $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.8-7.4 (5H, m), 6.32 (1H, d, J 1 Hz), 5.91 (1H, d, J 1 Hz), 3.5 (2H,**

s), and 0.45 (6H, s), $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 148.13, 139.23, 134.14, 129.27, 127.96, 133.88, 28.89, and -1.98.

2-Dimethyl(phenyl)silylmethylprop-2-enol (20a).—Formaldehyde vapour, from heating paraformaldehyde, was passed over the lithium reagent **17** (6.5 mmol) at dry-ice/acetone temperatures and the mixture stirred for 1 h, brought to 0 °C, and stirred for 1 h. Workup and chromatography (SiO_2 , Et_2O -hexane, 2:7) gave the alcohol (337 mg, 82%) (Found: C, 69.7; H, 8.7. $\text{C}_{12}\text{H}_{18}\text{OSi}$ requires C, 69.8; H, 8.8%) IR(film) 3360 and 890 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.6-7.3 (5H, m), 4.91 (1H, br s), 4.68 (1H, br s), 3.94 (2H, br s), 1.78 (2H, s), and 0.37 (6H, s), $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 147.19, 133.65, 129.28, 127.91, 107.75, 67.13, 22.70, and -2.90.

2-Methyl-3-dimethyl(phenyl)silylmethylbut-3-en-2-ol (20b).—Acetone (1 ml) was added to the lithium reagent **17** (2 mmol) at -30 °C and the mixture stirred for 2 h, brought to 0 °C, and stirred for 30 min. Workup and chromatography (SiO_2 , Et_2O -hexane, 2:7) gave the alcohol (318 mg, 68%) (Found: C, 71.9; H, 9.6. $\text{C}_{14}\text{H}_{22}\text{OSi}$ requires C, 71.7; H, 9.5%) IR(film) 3480 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.75-7.4 (5H, m), 5.05 (1H, d, J 1 Hz), 4.75 (1H, d, J 1 Hz), 2.05 (2H, s), 1.4 (6H, s), and 0.47 (6H, s).

2-Dimethyl(phenyl)silylmethylhexa-2,4-dien-3-ol (21).—Crotonaldehyde (170 mg, 2.4 mmol) in THF (2.5 ml) was added to the lithium reagent **17** (2 mmol) at -30 °C and the mixture stirred for 2 h, brought to 0 °C, and stirred for 30 min. Workup and chromatography (SiO_2 , Et_2O -hexane, 1:7) gave the alcohol (389 mg, 79%) (Found: C, 73.3; H, 9.15. $\text{C}_{15}\text{H}_{22}\text{OSi}$ requires C, 73.1; H, 9.0%) IR(film) 3450, 1640, and 975 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 7.7-7.4 (5H, m), 5.9-5.55 (2H, m), 5.15 (1H, m), 4.8 (1H, m), 4.4 (1H, d, J 7 Hz), 2.0 (2H, s), 1.9 (3H, d, J 6 Hz), 1.5 (1H, br s), and 0.45 (6H, s).

Protodesilylation of the Vinylsilanes 32 and 39.—The vinylsilane (1.4 mmol) and hydriodic acid (0.12 ml) were stirred in benzene (1 ml) at room temperature for 1 h. Work up gave (*Z*)-1-phenylpropene and (*Z*)-hept-2-ene with definitive spectra.²⁷

Allylation of the Products of Stannyl-Cupration.—Allylations were carried out with the appropriate allyl bromide in a similar way to the methylations described above. The following compounds were prepared in this way: **2-Tributylstannylhexa-1,5-diene** (81%) IR(film) 1635 and 1620 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 6.1-5.6 and 5.2-4.5 (5H, m) and 2.2-0.8 (31H, m), m/z 372 (0.1%, M^+), 315 (100), and 291 (88). **2-Methyl-6-tributylstannylhepta-2,6-diene** (81%) IR(film) 935 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 5.69 (1H, dt, J 2.8 and 1.4 Hz), 5.2-5.0 (2H, m), 2.4-1.8 (4H, m), 1.69 (3H, br s), 1.61 (3H, br s), and 1.6-0.7 (27H, m), m/z 399 (0.5%, M^+), 343 (100), and 291 (88). **2-Methyl-3-tributylstannylmethylhexa-2,6-diene** (84%) IR(film) 1635 and 1620 cm^{-1} , $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 5.77 (1H, ddt, J 9.4, 17.4, and 6.2 Hz), 5.1-4.8 (2H, m), 2.69 (2H, br d, J 6.2 Hz), 1.71 (2H, s), 1.67 (3H, s), 1.62 (3H, s), and 1.7-0.7 (27H, m), m/z 400 (5%, M^+), 343 (9), and 291 (100).

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