Silyl-cupration of an acetylene followed by ring-formation

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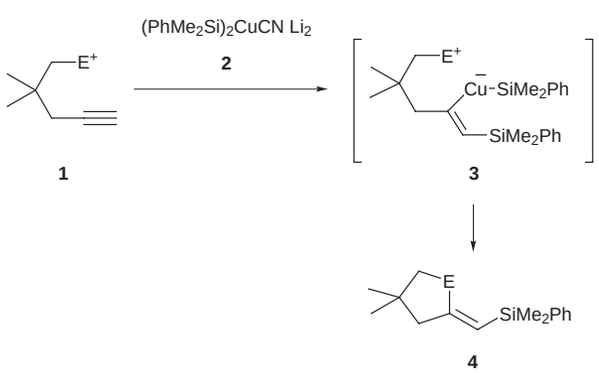
The acetylenes **1a**–**e** undergo silyl-cupration followed by cyclisation, the acetylenes **1f**–**1h** react with the silyl-cuprate reagent more rapidly at the alternative electrophilic site, and the acetylenes **1i**, **1j** and **17** give relatively low yields of cyclic products amongst others. Ring-formation is, unusually, a not particularly favourable pathway.

Introduction

We established in a series of papers between 1978[1] and 1995 that our phenyldimethylsilylcuprate reagent **2**[2] reacts with acetylenes,[3] allenes,[4] allylic acetates[5] and a variety of αβ-unsaturated enone systems.[6] Others have established that the same or similar silyl-cuprate reagents react with acid chlorides,[7,8] allylic chlorides,[9] a vinyl iodide,[10] epoxides,[8,11] a primary alkyl bromide,[11] an iminium ion,[12] a vinyl sulfone,[13] vinyl sulfoxides,[14] and a few other, probably less general, functional groups.[15] However, we had almost no indication what the *relative* reactivity of these substrates might be. Allyl crotonate gave conjugate addition of the silyl-cuprate reagent to the enone system and only a little crotonic acid from cleavage of the allyl ester function,[16] but allyl cinnamate gave largely cinnamic acid,[17] from which we deduce that αβ-unsaturated esters and primary allylic acetates are comparable in reactivity. The only other hint was that Oshima had observed 3–6-membered ring-formation in the copper-catalysed addition of $PhMe_2SiMgMe$ to terminal acetylenes carrying a range of primary and secondary methanesulfonate and tosylate (toluene-*p*-sulfonate) groups, in which the first step had been the attack on the acetylene group rather than on the carbon carrying the sulfonate groups.[18] We already knew that the reaction with a terminal acetylene[3] was one of the easiest to do, and that it took place at low temperature. We chose, therefore, to investigate the reaction of a terminal acetylene **1** attached by a chain of three or four carbon atoms to several of the other groups, labelled E^+ (Scheme 1). We hoped that, when the

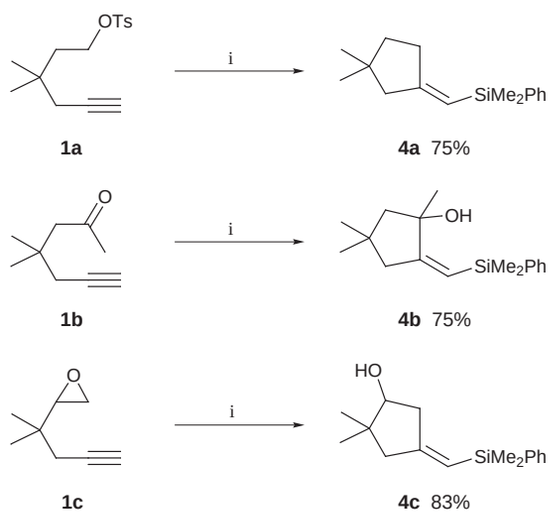


Scheme 1

acetylene was the site of initial attack, carbocyclic rings **4** might be formed from an intermediate vinylcuprate **3**, and, when it was not, we would at least learn something about the relative reactivity of the various groups. We reported some of our work in a preliminary communication,[19] and we now report it in full.

Results and discussion

We begin with the reactions carried out in the easier way, by adding the substrates **1** to the bissilylcuprate reagent **2**. The most simple of these (Scheme 2) showed that the acetylene was

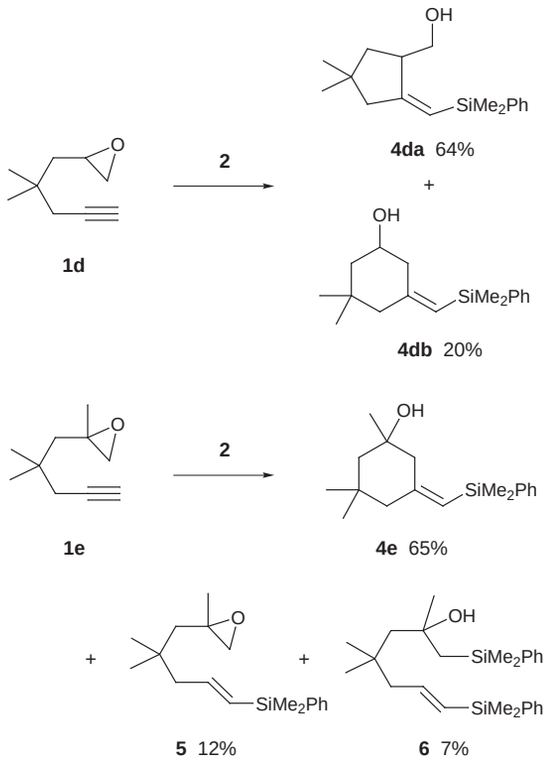


Scheme 2 *Reagents*: i, $(PhMe_2Si)_2CuCNLi_2$, THF, −78 °C→room temp., normal addition.

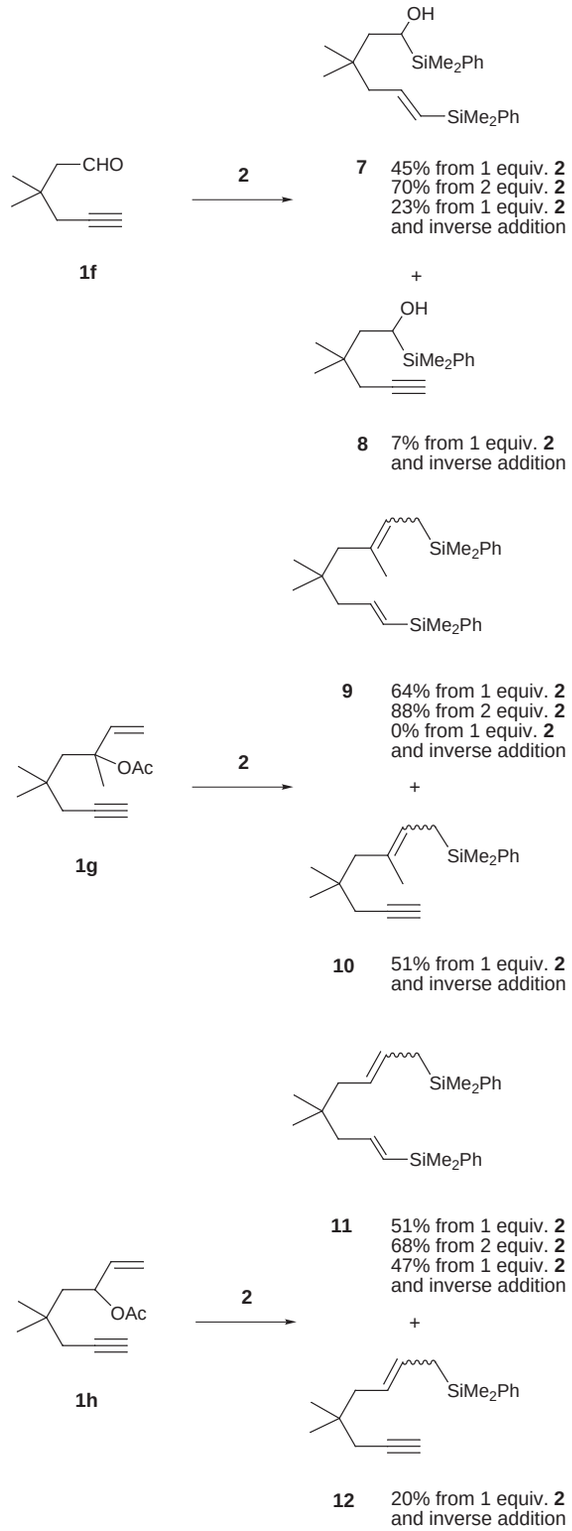
more reactive than the toluene-*p*-sulfonate, the ketone, and the epoxide groups in the substrates **1a**–**1c**, giving the cyclopentanes **4a**–**4c** as the only identifiable products.

The epoxides **1d** and **1e** were only slightly more complicated (Scheme 3), giving a mixture of regioisomers **4da** and **4db** in the former case, and a mixture of three products in the latter: the major product was the six-membered ring cyclisation product **4e**, but there were minor amounts of the product **5** of silyl-cupration without cyclisation, and of the product **6** of reaction at both sites. The proportion of reaction taking place at both sites should be reduced by inverse addition, although this is somewhat less convenient to carry out, and runs a small risk of losing, through decomposition, some of the silyl-cuprate reagent as it is transferred by cannula into the cold solution of the substrate. However, inverse addition in the reaction with the epoxide **1e** did not increase the amount of the cyclic product **4e**: the three products were formed in yields of 44%, 41% and 10%, respectively, raising the proportion of reaction taking place without cyclisation, possibly because the intermediate **3** is generated in a less scrupulously dry medium.

In contrast, the aldehyde **1f** and the allylic acetates **1g** and **1h** gave no cyclic product (Scheme 4). When we used one equivalent of the bissilylcuprate **2** on the aldehyde **1f**, the only recognisable product, apart from some recovered aldehyde, was the alcohol **7** (45%) from attack at both sites. With two equivalents of the cuprate, the yield of this product was quite good (70%). Using inverse addition, we were able to isolate a small amount of the alcohol **8**, showing that the aldehyde group was more



Scheme 3



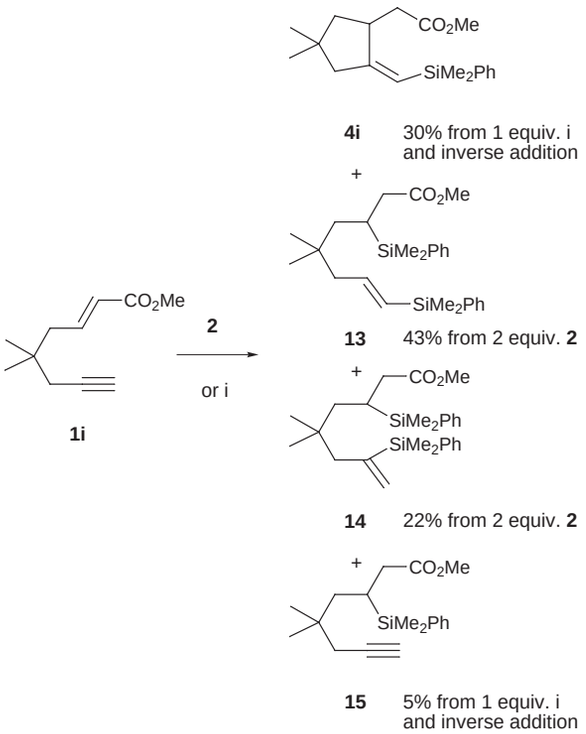
Scheme 4

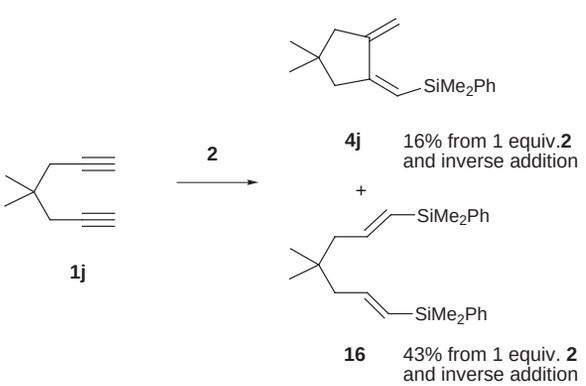
reactive than the acetylene group. Similarly, the allylic acetates **1g** and **1h**, with either one or two equivalents of the cuprate reagent, gave largely the allylsilanes **9** and **11**, as mixtures of geometrical isomers, from attack at both sites. Using inverse addition, we were able to isolate the mixtures of allylsilanes **10** and **12**, respectively, in which no reaction had occurred at the acetylene groups, showing that allylic acetates are also more reactive than a terminal acetylene. In the reactions with the allylic acetates, we also obtained substantial amounts of unchanged starting material, but there was no sign in any of these experiments of any significant quantities of cyclic products. There is therefore little hope of using an aldehyde or an allylic acetate for ring formation by this method.

The αβ-unsaturated ester **1i** and the acetylene **1j** each gave some cyclisation (Scheme 5). Because the former might be one of the more useful synthetic reactions we carried it out under a number of different conditions and with a number of silyl-cuprate reagents. The cyclopentane **4i** was present in the product mixture of every variant that we tried, except when we used two equivalents of the cuprate **2** and normal addition, when we obtained the product **13** of addition at both sites, together with its regioisomer **14** having the silyl group attached to the internal carbon atom of the acetylene. The best yield of the cyclisation product **4i** was a mere 30% (60% based on starting material consumed) obtained using one equivalent of a 1 : 1 silyl-cuprate reagent and inverse addition, which this time did increase the proportion of cyclisation. It appears that the unsaturated ester group is nearly as reactive as the acetylene group, as shown by the formation of some of the product **15** of reaction only at that site. A similar cyclisation has been achieved with a stannyl cuprate.[20]

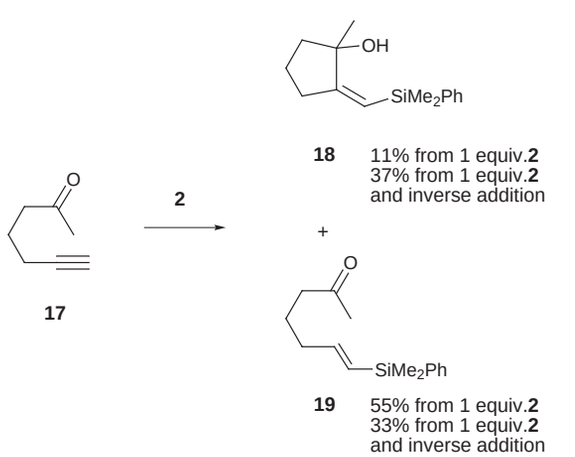
Why do we see here such a limited range of substrates undergoing cyclisation, when five-membered ring formation is normally faster than intermolecular reactions? We believe that silyl-cuprates are inherently more reactive than carbon-based cuprates, based on our observation that a mixed cuprate, having one silyl group and one alkyl, transfers only the silyl group to any of the usual substrates.[21] In consequence, the intramolecularity of the cyclisation step **3**→**4** must compete with the relatively high reactivity of silyl-cuprates in the intermolecular reaction. We were not too surprised therefore that cyclisation might not always occur, even when the acetylene was the first group to be attacked by the silyl-cuprate reagent.

Because we foresaw that cyclisation might not be easy, we had incorporated geminal dimethyl groups in all the substrates **1** above, in order to benefit from the Thorpe–Ingold effect. In Oshima's reaction, similar to **1a**→**4a** but with no geminal dimethyl group, cyclisation had been easy, but we reasoned that this was an especially favourable situation. That it had been a wise precaution for our other reactions became evident when we repeated the second of our most successful reactions without that advantage. In contrast to the ketone **1b**, the ketone **17**





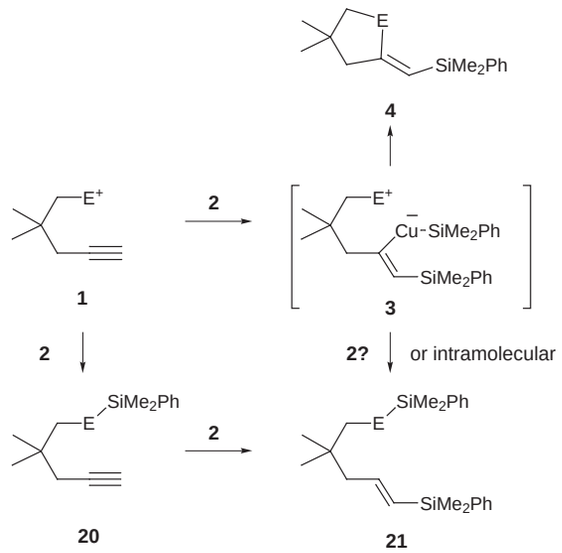
Scheme 5 *Reagent*: i, $PhMe_2SiCuCNLi$.



Scheme 6

gave two recognisable products **18** and **19** (Scheme 6). The alcohol **18** was only a minor component under normal conditions, and not even the only product using inverse addition, although the yield was raised to 37%. Ring-formation clearly needs all the help it can get.

There are two routes to the products of double addition **21**



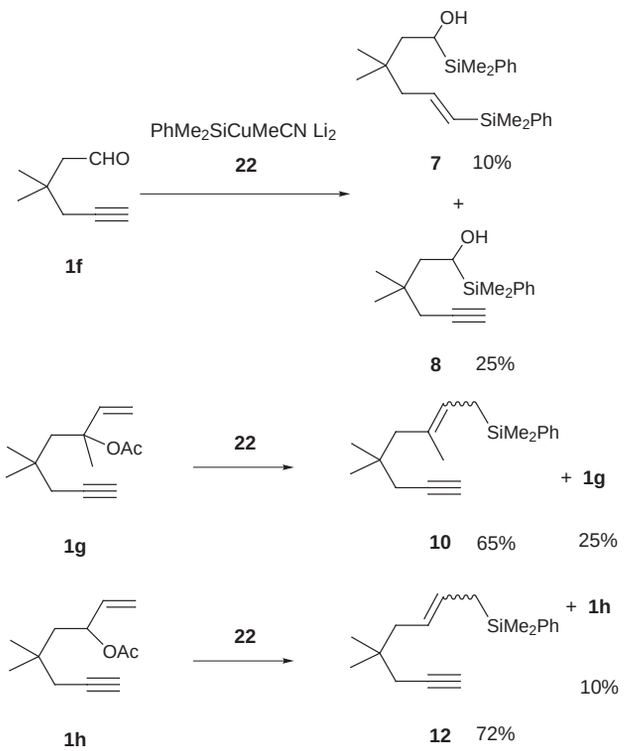
Scheme 7

(Scheme 7). In the one, the silyl-cuprate reagent attacks the group E^+ to give an intermediate **20** faster than it attacks the acetylene to give an intermediate **3**. This is the route we believe is followed in the reactions with the aldehyde **1f**, the allylic acetates **1g** and **1h**, and perhaps with the unsaturated ester **1i**. In the other, those substrates reacting first at the acetylene group, such as the epoxide **1e**, perhaps the unsaturated ester **1i**, and the bisacetylene **1j**, evidently do not always undergo cyclisation **3**→**4** faster than the delivery of a silyl group to the group E^+. In the latter case, the second silyl group might be delivered to the group E^+ by intermolecular attack on the intermediate **3** or by intramolecular delivery of the silyl group already present in the mixed cuprate functionality. With simple acetylenes, the addition of electrophiles to the first-formed product of silylcupration, analogous to **3**, has always given the products of carbon–carbon bond formation,[3] similar to the step **3**→**4**. However, other mixed cuprates, prepared from one equivalent of the silyllithium reagent and one equivalent of an alkyllithium reagent, regularly give products of silicon–carbon bond formation.[21] We have commented before on this unexplained discrepancy, and hoped that some of the work in this paper might throw light upon it. Certainly, we cannot discount the possibility here of intramolecular delivery of the silyl group in the step **3**→**21**, which might explain the inefficiency of the cyclisation.

If **3**→**21** is a bimolecular reaction, inverse addition ought to reduce the ratio **21**:**4** when compared with normal addition. Alternatively, if the silyl group is transferred intramolecularly, the ratio **21**:**4** should be unaffected. In the reaction using inverse addition with the unsaturated ester **1i**, the ratio decreased, which implied that intramolecular delivery is not occurring. In one other reaction, **1e**→**4e**–**6**, the proportion of bis-adduct was essentially the same using inverse addition, but that could simply have been a consequence of protonation, before the second attack took place.

A second test was to examine the pattern of reactivity of the bissilyl-cuprate **2** and the mixed cuprate **22**. With this cuprate, the intermediate corresponding to **3** would carry a carbon ligand on the copper in place of the silyl, and any formation of the bis-adduct **21** would have to be intermolecular, unless it were the result of ligand exchange followed by intramolecular delivery. This reagent might also show different chemoselectivity, allowing cyclisation where it had not occurred before.

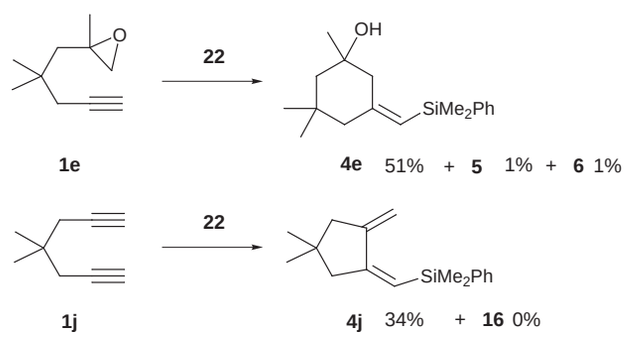
Using normal addition, adding the aldehyde **1f** and the allylic acetates **1g** and **1h** to the mixed cuprate **22** gave higher yields of the alcohol **8** and the allylsilanes **10** and **12** (Scheme 8) than we obtained in the earlier work. In the reactions with the allylic acetates, we again obtained substantial amounts of unchanged



Scheme 8

starting material, and in all three cases there was no trace of cyclisation. We conclude that the mixed cuprate is simply more selective overall than the bissilyl-cuprate.

With two of the reactions that had shown some cyclisation, the epoxide **1e** now showed a drop in the amount of bis-adduct **6** from 7% to 1%, and the bis-acetylene **1j** showed a drop in the amount of bis-adduct **16** from 43% to 0% (Scheme 9). The last

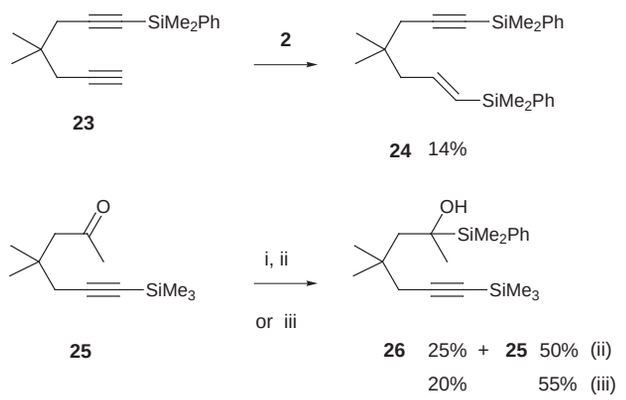


Scheme 9

result is the only one striking enough to suggest that intramolecular delivery of the silyl group might have been occurring, but there is an alternative explanation: if the mixed cuprate **22** is less reactive than the homocuprate **2**, as we suspect from its greater selectivity, then the intermediate analogous to **3** will have more time in which to cyclise. With the remaining reaction that showed some cyclisation, the αβ-unsaturated ester **1i** giving the ester **4i**, the mixed cuprate **22** gave none of the cyclisation product **4i** and only a little more (8%) of the product **15** of attack only at the αβ-unsaturated ester group.

We conclude that the mixed cuprate **22** has some perhaps usefully different chemoselectivity, probably by virtue of its lower reactivity, and that there is no compelling evidence for intramolecular delivery of the silyl group to the electrophilic centre in any of the intermediates **3**. The puzzle remains: why mixed cuprates like **3** should react at the vinyl group both intermolecularly[21] and intramolecularly, as here, and not at the silyl, when the mixed cuprate **22** delivers the silyl group rather than the methyl?

With little prospect of achieving cyclisation, we did try one other pair of functional groups, setting a silylated terminal acetylene against a terminal acetylene **23** and against a ketone group **25** (Scheme 10). We already knew that silylated terminal



Scheme 10 *Reagents*: i, $BF_3{\cdot}OEt_2$; ii, $(PhMe_2Si)_2CuCNLi_2$; iii, $PhMe_2SiLi$.

acetylenes react with the silyl-cuprate reagent to place, *syn* stereospecifically, the silyl group on the internal carbon and the copper on the silylated carbon.[22] This intermediate cannot form a ring by attacking the other functional group unless it does so with inversion of configuration at the copper-bearing carbon. In the event there was no cyclisation, and we obtained in low yield only the product **24** of silylcupration of the terminal acetylene. The ketone **25** showed no reaction with the silyl-cuprate alone, but it did react at the ketone group in the presence of boron trifluoride–diethyl ether. In this, it was little different from the silyllithium reagent, which gave the same alcohol **26** in comparably low yield.

Except for the epoxide **1c**, which we prepared from the aldehyde **29**, we prepared all the substrates **1** from the ketone **1b**, which is the product of an Eschenmoser fragmentation starting from isophorone. The routes used are summarised in Scheme 11. The ketone **17**, likewise, was the product of an Eschenmoser fragmentation starting from cyclohexenone.

Experimental

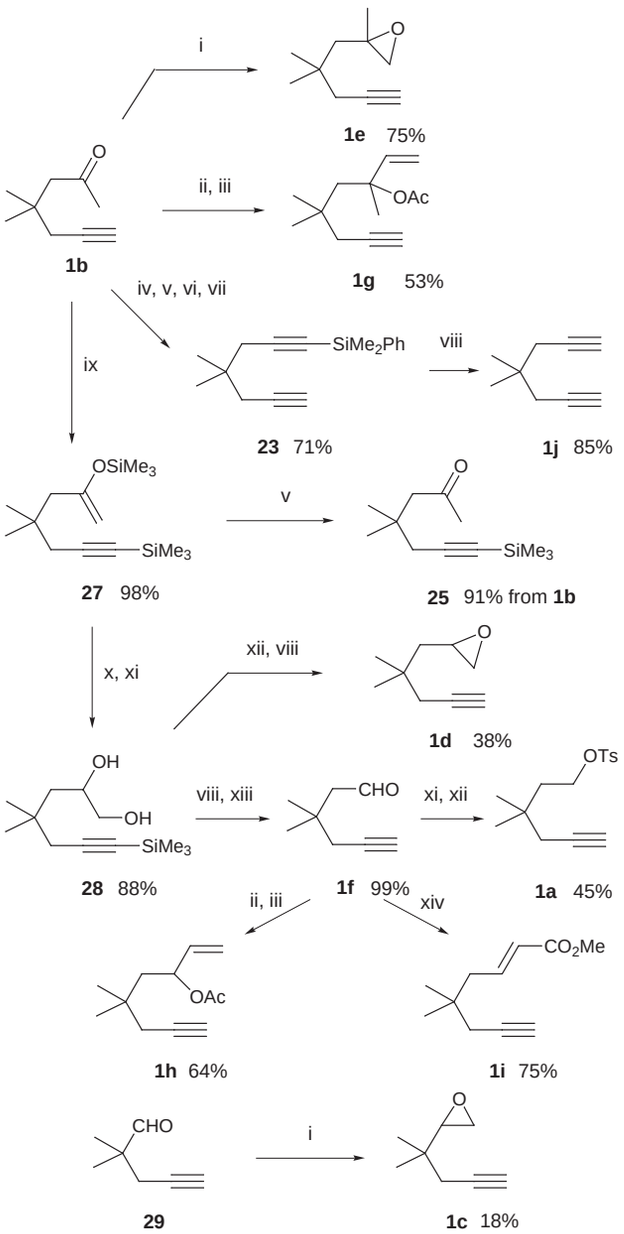
Light petroleum refers to the fraction bp 30–40 °C and ether refers to diethyl ether. *J* Values are given in Hz.

Silyl-cupration reactions

Method A (normal addition). Typically, the substrate (1 mmol) in dry THF (2 cm^3) was added dropwise over 10 min at −78 °C to lithium bis[dimethyl(phenyl)silyl]cuprate[3] [0.7–1.2 mol dm^{-3} in THF, 2.2 mmol, prepared from copper(I) cyanide] and the mixture stirred at −78 °C for 2–4 h. The mixture was allowed to warm slowly to room temperature, quenched with basic ammonium chloride solution (5 cm^3), filtered through Celite and extracted with ether (3 × 10 cm^3). The organic extracts were combined, washed with basic ammonium chloride solution (3 × 10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography.

Method B (inverse addition). Typically, the silyl-cuprate was added dropwise through a cannula (15 cm) to the substrate (1 mmol) in dry THF (2 cm^3) under argon at −78 °C. The mixture was stirred at −78 °C for 2–4 h and worked up as in Method A.

Method C (mixed methylsilyl cuprate). Typically, dimethyl-



Scheme 11 *Reagents*: i, CH_2Br_2, BuLi; ii, CH_2=CHMgBr; iii, Ac_2O, DMAP; iv, LDA, $PhMe_2SiCl$; v, H_3O^+; vi, LDA, $(EtO)_2POCl$; vii, LDA; viii, TBAF; ix, LDA, Me_3SiCl; x, MCPBA; xi, $NaBH_4$; xii, TsCl, DMAP; xiii, $NaIO_4$; xiv, Ph_3P=$CHCO_2Me$.

(phenyl)silyllithium (0.7–1.2 mol dm^{-3} in THF, 1.1 mmol) and methyllithium (1.0–1.6 mol dm^{-3} in THF, 1.1 mmol) were added in succession to a stirred suspension of copper(I) cyanide (1.15 mmol) in dry THF (2–3 cm^3) under argon at 0 °C, and stirred for an additional 0.5 h. This reagent was then used as in Methods A and B above.

The following compounds were prepared in one or more of these ways.

(*E*)-1-[Dimethyl(phenyl)silyl]methylidene-3,3-dimethylcyclopentane 4a. Compound **4a** (75%) was prepared from the tosylate **1a** (1.1 mmol) by Method A (experiment carried out by Klaus Breuer); R_f (hexane) 0.62; ν_{max}(film)/cm^{-1} 1621 (C=C), 1246 (SiMe), 1111 (SiPh) and 839 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.56–7.48 (2 H, m, *o*-SiArH), 7.37–7.32 (3 H, m, *p*- and *m*-SiArH), 5.49 (1 H, t, *J* 2.2, SiCH=C), 2.25 (2 H, br t, *J* 7.6, CH_2CH_2C=C), 2.18 (2 H, br s, Me_2CCH_2C=C), 1.47 (2 H, t, *J* 7.6, CH_2CH_2C=C), 0.97 (6 H, s, Me_2C) and 0.33 (6 H, s, Me_2Si). This compound rearranges on prolonged contact with silica gel to give a mixture of unidentified compounds with vinyl protons in the ^{1}H-NMR spectrum, probably the endocyclic double bond isomers.

(*Z*)-2-[Dimethyl(phenyl)silyl]methylidene-1,4,4-trimethylcyclopentanol 4b. Compound **4b** (75%) was prepared from the ketone **1b** (11 mmol) by Method A (experiment first carried out by Helen Hailes); R_f (Et_2O–hexane, 1:9) 0.25; ν_{max}(film)/cm^{-1} 3580 and 3480 (OH), 1645 (C=C), 1250 (SiMe), 1115 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.60–7.55 (2 H, m, *o*-SiArH), 7.40–7.33 (3 H, m, *p*- and *m*-SiArH), 5.54 (1 H, m, CH=C), 2.44 (1 H, dd, *J* 2.3 and 15.2, CH_AH_BC=C), 2.14 (1 H, d, *J* 15.1, CH_AH_BC=C), 1.72 (1 H, d, *J* 13.7, CH_AH_BCOH), 1.60 (1 H, d, *J* 12.9, CH_AH_BCOH), 1.25 (1 H, s, *Me*COH), 1.23 (1 H, s, OH), 1.02 (3 H, s, Me_AMe_BC), 0.99 (3 H, s, Me_AMe_BC), 0.47 (3 H, s, Me_AMe_BSi) and 0.38 (3 H, s, Me_AMe_BSi); δ_C($CDCl_3$) 170.1, 141.2, 133.7, 128.9, 127.9, 119, 79.5, 57.5, 52.7, 34.7, 30.1, 29.9, 29.7, 0.4 and −0.4 (Found: C, 74.55; H, 9.6. $C_{17}H_{26}OSi$ requires C, 74.4; H, 9.55%). A nuclear Overhauser enhancement (NOE) was observed at δ 2.14 by irradiating the signals at δ 5.54 and at δ 2.44, and at δ 2.44 and δ 5.54 by irradiating at δ 2.14, confirming the double bond geometry. The *acetate* of this alcohol was prepared (15%) by the method of Höfle and Steglich;[23] R_f (EtOAc–hexane, 1:9) 0.53; ν_{max}(film)/cm^{-1} 1740 (C=O), 1635 (C=C), 1250 (SiMe), 1115 (SiPh) and 835 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.58–7.53 (2 H, m, *o*-SiArH), 7.32–7.30 (3 H, m, *p*- and *m*-SiArH), 5.60 (1 H, m, CH=C), 2.41 (1 H, dd, *J* 2.2 and 15.2, CH_AH_BC=C), 2.24 (1 H, d, *J* 15.2, CH_AH_BC=C), 2.13 (1 H, d, *J* 14.7, CH_AH_BCOH), 2.03 (1 H, d, *J* 14.5, CH_AH_BCOH), 1.64 (3 H, s, $MeCO_2$), 1.57 (3 H, s, *Me*COAc), 1.04 (3 H, s, Me_AMe_BC), 1.02 (3 H, s, Me_AMe_BC), 0.41 (3 H, s, Me_AMe_BSi) and 0.36 (3 H, s, Me_AMe_BSi) (Found: C, 71.95; H, 8.9. $C_{19}H_{28}O_2Si$ requires C, 72.1; H, 8.9%).

(*Z*)-4-[Dimethyl(phenyl)silyl]methylidene-2,2-dimethylcyclopentanol 4c. Compound **4c** (83%) was prepared from the epoxide **1c** (0.69 mmol) by Method A; R_f (EtOAc–hexane, 1:9) 0.11; ν_{max}(film)/cm^{-1} 3350 (OH), 1625 (C=C), 1251 (SiMe), 1115 (SiPh) and 829 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.54–7.49 (2 H, m, *o*-SiArH), 7.35–7.31 (3 H, m, *p*- and *m*-SiArH), 5.53 (1 H, t, *J* 2.2, CH=C), 3.76 (1 H, br t, *J* 6.0, C*H*OH), 2.59 (1 H, ddd, *J* 2.3, 6.7 and 18.0, CH_AH_BCHOH), 2.39 (1 H, br d, *J* 16.4, $Me_2CCH_AH_B$), 2.19 (1 H, br d, *J* 15.7, $Me_2CCH_AH_B$), 2.16 (1 H, dd, *J* 5.8 and 18.2, CH_AH_BCOH), 1.89 (1 H, br s, OH), 0.95 (3 H, s, Me_AMe_BC), 0.94 (3 H, s, Me_AMe_BC), 0.34 (3 H, s, Me_AMe_BSi) and 0.33 (3 H, s, Me_AMe_BSi).

(*Z*)-{2-[Dimethyl(phenyl)silyl]methylidene-4,4-dimethylcyclopentyl}methanol 4da. Compound **4da** (64%) was prepared from the epoxide **1d** (0.75 mmol) by Method A; R_f (EtOAc–hexane, 1:9) 0.20; ν_{max}(film)/cm^{-1} 3364 (OH), 1638 (C=C), 1248 (SiMe), 1113 (SiPh) and 833 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.52–7.48 (2 H, m, *o*-SiArH), 7.37–7.32 (3 H, m, *p*- and *m*-SiArH), 5.09 (1 H, s, C=CHSi), 3.49 (2 H, d, *J* 4.7, CH_2OH), 2.55 (1 H, br s, $CHCH_2OH$), 1.80 (1 H, br d, *J* 14.0, CH_AH_BC=C), 1.75 (1 H, dd, *J* 8.3 and 12.8, CH_AH_BCH), 1.62 (1 H, br d, *J* 14.0, CH_AH_BC=C), 1.48 (1 H, dd, *J* 6.9 and 12.8, CH_AH_BCH), 1.04 (3 H, s, Me_AMe_BC), 0.96 (3 H, s, Me_AMe_BC), 0.31 (3 H, s, Me_AMe_BSi) and 0.30 (3 H, s, Me_AMe_BSi) (Found: C, 74.6; H, 9.75. $C_{17}H_{26}OSi$ requires C, 74.4; H, 9.55%).

(*Z*)-5-[Dimethyl(phenyl)silyl]methylidene-3,3-dimethylcyclohexanol 4db. Compound **4db** (20%) was also prepared from epoxide **1d**; R_f (EtOAc–hexane, 1:9) 0.20; ν_{max}(film)/cm^{-1} 3342 (OH), 1618 (C=C), 1248 (SiMe), 1112 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.57–7.51 (2 H, m, *o*-SiArH), 7.36–7.31 (3 H, m, *p*- and *m*-SiArH), 5.37 (1 H, s, C=CHSi), 3.58 (1 H, tt, *J* 4.6 and 10.8, C*H*OH), 2.63 (1 H, ddt, *J* 1.7, 4.6 and 12.3, $CH(OH)CH_{eq}H_{ax}C$=C), 2.03 (1 H, br d, *J* 12.8, $Me_2CCH_{eq}H_{ax}C$=C), 1.91 (1 H, br d, *J* 12.8, $Me_2CCH_{eq}H_{ax}C$=C), 1.76 (1 H, br t, *J* 11.8, $CH(OH)CH_{eq}H_{ax}C$=C), 1.69 (1 H, ddt, *J* 2.0, 4.1

and 12.5, $Me_2CCH_{eq}H_{ax}CHOH$), 1.20 (1 H, br t, *J* 12.2, $Me_2CCH_{eq}H_{ax}CHOH$), 0.98 (3 H, s, Me_AMe_BC), 0.85 (3 H, s, Me_AMe_BC), 0.37 (3 H, s, Me_AMe_BSi) and 0.35 (3 H, s, Me_AMe_BSi) (Found: M^+, 274.1753. $C_{17}H_{26}OSi$ requires *M*, 274.1752). A minor product was also isolated and tentatively assigned the structure *(E)-1,7-bis[dimethyl(phenyl)silyl]-4,4-dimethylhept-6-en-2-ol* (3%); R_f (EtOAc–hexane, 1:9) 0.30; ν_{max}(film)/cm^{-1} 3405 (OH), 1251 (SiMe), 1115 (SiPh) and 832 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.53–7.49 (2 H, m, *o*-SiArH), 7.35–7.32 (3 H, m, *p*- and *m*-SiArH), 6.08 (1 H, dt, *J* 7.0 and 18.4, CH=CSi), 5.73 (1 H, d, *J* 18.4, C=CHSi), 3.98 (1 H, m, C*H*OH), 2.03 (2 H, br d, *J* 6.9, CH_2C=C), 1.26 (2 H, m, Me_2CCH_2COH), 1.08 (1 H, dd, *J* 7.7 and 14.7, CH_AH_BSi), 0.99 (1 H, dd, *J* 6.0 and 14.7, CH_AH_BSi), 0.90 (3 H, s, Me_AMe_BC), 0.87 (3 H, s, Me_AMe_BC), 0.321 (6 H, s, Me_2Si_A) and 0.319 (6 H, s, Me_2Si_B).

(*Z*)-5-[Dimethyl(phenyl)silyl]methylidene-1,3,3-trimethylcyclohexanol 4e. Compound **4e** (65%) was prepared from the epoxide **1e** (4.7 mmol) by Method A, (44%) from the epoxide **1e** (1.3 mmol) by Method B, and (51%) from the epoxide **1e** (3.3 mmol) by Method C, which also gave recovered epoxide (12%); R_f (EtOAc–hexane, 1:9) 0.22; ν_{max}(film)/cm^{-1} 3600 and 3480 (OH), 1630 (C=C), 1250 (SiMe), 1115 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.60–7.54 (2 H, m, *o*-SiArH), 7.41–7.33 (3 H, m, *p*- and *m*-SiArH), 5.48 (1 H, d, *J* 1.0, CH=C), 2.28 (1 H, dd, *J* 1.5 and 13.9, C=C$CH_{eq}H_{ax}$COH), 2.03 (1 H, masked br d, C=C$CH_{eq}H_{ax}$COH), 2.01 (2 H, br s, Me_2CCH_2C=C), 1.51 (1 H, dd, *J* 0.8 and 14.1, $Me_2CCH_{eq}H_{ax}COH$), 1.32 (1 H, d, *J* 14.1, $Me_2CCH_{eq}H_{ax}COH$), 1.06 (3 H, s, *Me*COH or Me_AMe_BC), 1.00 (3 H, s, *Me*COH or Me_AMe_BC), 0.92 (3 H, s, *Me*COH or Me_AMe_BC), 0.87 (1 H, s, OH), 0.41 (3 H, s, Me_AMe_BSi) and 0.39 (3 H, s, Me_AMe_BSi) (Found: C, 74.7; H, 9.65. $C_{18}H_{28}OSi$ requires C, 74.95; H, 9.8%).

(*E*)-1-{5-[Dimethyl(phenyl)silyl]-2,2-dimethylpent-4-enyl}-1-methyloxirane 5. Compound **5** (12%) was prepared by Method A. (41%) Method B, and (1%) Method C; R_f (EtOAc–hexane, 1:9) 0.37; ν_{max}(film)/cm^{-1} 1610 (C=C), 1245 (SiMe), 1110 (SiPh) and 835 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.53–7.47 (2 H, m, *o*-SiArH), 7.37–7.30 (3 H, m, *p*- and *m*-SiArH), 6.09 (1 H, dt, *J* 18.5 and 7.0, CH=CSi), 5.77 (1 H, dt, *J* 18.4 and 1.1, C=CHSi), 2.60 (1 H, dd, *J* 0.4 and 4.9, CH_AH_BO), 2.57 (1 H, dd, *J* 1.2 and 4.9, CH_AH_BO), 2.14 (1 H, ddd, *J* 1.2, 7.0 and 13.4, CH_AH_BC=C), 2.12 (1 H, ddd, *J* 1.2, 7.0 and 13.4, CH_AH_BC=C), 1.73 (1 H, dd, *J* 1.2 and 14.2, CH_AH_BCO), 1.38 (3 H, s, MeCO), 1.28 (1 H, br d, *J* 14.1, CH_AH_BCO), 1.00 (3 H, s, Me_AMe_BC), 0.97 (3 H, s, Me_AMe_BC) and 0.32 (6 H, s, Me_2Si) (Found: C, 74.95; H, 9.95. $C_{18}H_{28}OSi$ requires C, 74.95; H, 9.8%).

(*E*)-1,7-Bis[dimethyl(phenyl)silyl]-2,4,4-trimethylhept-6-en-2-ol 6. Compound **6** (7%) was prepared by Method A, (10%) Method B, and (1%) Method C; R_f (EtOAc–hexane, 1:9) 0.27; ν_{max}(film)/cm^{-1} 3580 and 3475 (OH), 1610 (C=C), 1245 (SiMe), 1110 (SiPh) and 825 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.56–7.52 (2 H, m, *o*-SiArH), 7.37–7.33 (3 H, m, *p*- and *m*-SiArH), 6.14 (1 H, dt, *J* 18.5 and 7.0, CH=CSi), 5.77 (1 H, d, *J* 18.5, C=CHSi), 2.14 (2 H, dd, *J* 1.0 and 7.0, CH_2C=C), 1.52 (1 H, d, *J* 14.9, $Me_2CCH_AH_BCO$), 1.47 (1 H, d, *J* 14.9, $Me_2CCH_AH_BCO$), 1.32 (1 H, d, *J* 15.0, CH_AH_BSi), 1.29 (3 H, s, *Me*COH), 1.27 (1 H, d, *J* 15.3, CH_AH_BSi), 1.00 (3 H, s, Me_AMe_BC), 0.99 (3 H, s, Me_AMe_BC), 0.38 (6 H, s, Me_2Si_A) and 0.34 (6 H, s, Me_2Si_B) (Found: C, 73.3; H, 9.7. $C_{26}H_{48}OSi_2$ requires C, 73.5; H, 9.5%).

(*E*)-1,6-Bis[dimethyl(phenyl)silyl]-3,3-dimethylhex-5-en-1-ol 7. Compound **7** (45%) was prepared from the aldehyde **1f** (2.8 mmol) by Method A, (70%) from the aldehyde **1f** (1.48 mmol) by Method A, but using 2 equivalents of the silyl-cuprate, (23%) from the aldehyde **1f** (1.8 mmol) by Method B, and (10%) from the aldehyde **1f** (1.6 mmol) by Method C; R_f (EtOAc–hexane, 1:9) 0.20; ν_{max}(film)/cm^{-1} 3580 and 3460 (OH), 1610 (C=C), 1245 (SiMe), 1110 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.58–7.48 (2 H, m, *o*-SiArH), 7.39–7.31 (3 H, m, *p*- and *m*-SiArH), 6.07 (1 H, dt, *J* 7.0 and 18.5, CH=CSi), 5.75 (1 H, d, *J* 18.4, C=CHSi), 3.74 (1 H, dd, *J* 4.8 and 7.1, C*H*OH), 2.11 (2 H, d, *J* 6.9, CH_2C=C), 1.42 (2 H, m, CH_2COH), 0.92 (3 H, s, Me_AMe_BC), 0.89 (3 H, s, Me_AMe_BC) and 0.30 (6 H, s, Me_2Si) (Found: C, 72.85; H, 9.2. $C_{24}H_{36}OSi_2$ requires C, 72.65; H, 9.15%).

1-[Dimethyl(phenyl)silyl]-3,3-dimethylhex-5-yn-1-ol 8. Compound **8** (7%) was prepared by Method B, and (25%) Method C; R_f (EtOAc–hexane, 1:9) 0.15; ν_{max}(film)/cm^{-1} 3570 and 3470 (OH), 3300 (≡CH), 2110 (C≡C), 1250 (SiMe), 1110 (SiPh) and 835 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.59–7.52 (2 H, m, *o*-SiArH), 7.41–7.32 (3 H, m, *p*- and *m*-SiArH), 3.72 (1 H, dd, *J* 4.1 and 8.1, C*H*OH), 2.20 (1 H, dd, *J* 2.6 and 16.7, CH_AH_BC≡C), 2.13 (1 H, dd, *J* 2.7 and 16.7, CH_AH_BC≡C), 1.96 (1 H, t, *J* 2.7, HC≡C), 1.58 (1 H, dd, *J* 8.2 and 15.2, CH_AH_BCOH), 1.52 (1 H, dd, *J* 4.0 and 15.2, CH_AH_BCOH), 0.99 (6 H, s, Me_2C), 0.33 (3 H, s, Me_AMe_BSi) and 0.32 (3 H, s, Me_AMe_BSi) (Found: C, 73.25; H, 9.1. $C_{16}H_{24}OSi$ requires C, 73.8; H, 9.3%).

(1*E*,6*E*)- and (1*E*,6*Z*)-1,8-Bis[dimethyl(phenyl)silyl]-4,4,6-trimethylocta-1,6-diene 9. Compounds (1*E*,6*E*)-**9** and (1*E*,6*Z*)-**9** (64%, 7:1) were prepared from the acetate **1g** (2.4 mmol) by Method A, and (88%, 2:1) from the acetate **1g** (1.35 mmol) by Method A, but using 2 equivalents of the silyl-cuprate; R_f (hexane) 0.24; ν_{max}(film)/cm^{-1} 1615 (C=C), 1250 (SiMe), 1115 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) (major isomer, assigned tentatively as 6*E*) 7.54–7.50 (2 H, m, *o*-SiArH), 7.36–7.32 (3 H, m, *p*- and *m*-SiArH), 6.13 (1 H, dt, *J* 18.4 and 7.0, CH=CSi), 5.72 (1 H, d, *J* 18.4, C=CHSi), 5.13 (1 H, br t, *J* 8.4, C*H*=CMe), 2.02 (2 H, dd, *J* 0.8 and 7.0, CH_2C=CSi), 1.89 [2 H, s, Me_2CCH_2C(Me)=C], 1.67 (2 H, d, *J* 8.4, CH_2Si), 1.55 (3 H, s, MeC=C), 0.82 (6 H, s, Me_2C), 0.32 (6 H, s, Me_2Si_A) and 0.28 (6 H, s, Me_2Si_B) (minor isomer, assigned tentatively as 6*Z*) 7.53–7.47 (2 H, m, *o*-SiArH), 7.35–7.29 (3 H, m, *p*- and *m*-SiArH), 6.13 (1 H, dt, *J* 18.4 and 7.0, CH=CSi), 5.75 (1 H, d, *J* 18.5, C=CHSi), 5.28 (1 H, br t, *J* 8.3, C*H*=CMe), 2.08 (2 H, d, *J* 7.0, CH_2C=CSi), 1.88 [2 H, s, Me_2CCH_2C(Me)=C], 1.73 (3 H, s, MeC=C), 1.70 (2 H, d, *J* 8.3, CH_2Si), 0.88 (6 H, s, Me_2C), 0.31 (6 H, s, Me_2Si_A) and 0.24 (6 H, s, Me_2Si_B) (Found: C, 77.05; H, 9.65. $C_{27}H_{40}Si_2$ requires C, 77.05; H, 9.6%). In the run with one equivalent of the bissilyl-cuprate, starting acetate **1g** (10%) was obtained, together with a minor product assigned the structure *7-[dimethyl(phenyl)silyl]-3,5,5-trimethylocta-1,7-dien-3-yl acetate* (2%); R_f (EtOAc–hexane, 15:85) 0.55; ν_{max}(film)/cm^{-1} 1740 (C=O), 1250 (SiMe), 1110 (SiPh), 840 and 820 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.53–7.48 (2 H, m, *o*-SiArH), 7.34–7.30 (3 H, m, *p*- and *m*-SiArH), 5.87 (1 H, dd, *J* 11.0 and 17.5, C*H*=CH_2), 5.78 (1 H, d, *J* 2.9, CH_AH_B=CSi), 5.63 (1 H, d, *J* 2.9, CH_AH_B=CSi), 5.05 (1 H, dd, *J* 0.9 and 17.4, CH_AH_B=CH), 4.97 (1 H, dd, *J* 0.9 and 11.0, CH_AH_B=CH), 2.12 (2 H, m, CH_2C=C), 1.94 (3 H, s, $MeCO_2$), 1.57 (2 H, br s, CH_2COAc), 1.48 (3 H, s, *Me*COAc), 0.88 (3 H, s, Me_AMe_BC), 0.87 (3 H, s, Me_AMe_BC), 0.37 (3 H, s, Me_AMe_BSi) and 0.36 (3 H, s, Me_AMe_BSi).

(*E*)- and (*Z*)-8-[Dimethyl(phenyl)silyl]-4,4,6-trimethyloct-6-en-1-yne 10. Compounds (*E*)-**10** and (*Z*)-**10** (51%, 5:1) were prepared and starting acetate (44%) recorded from the acetate **1g** (1.03 mmol) by Method B, and (65%, 6:1) together with the starting acetate (25%) from the acetate **1g** (0.72 mmol) by Method C; R_f (hexane) 0.25; ν_{max}(film)/cm^{-1} 3310 (≡CH), 2120 (C≡C), 1250 (SiMe), 1115 (SiPh) and 835 (SiMe); δ_H(250 MHz; $CDCl_3$) (major isomer, assigned tentatively as *E*) 7.56–7.49 (2 H, m, *o*-SiArH), 7.36–7.30 (3 H, m, *p*- and *m*-SiArH), 5.21 (1 H, br t, *J* 8.5, C*H*=C), 1.99 (5 H, m, CH_2C≡C, *H*C≡C and Me_2CCH_2C=C), 1.67 (2 H, d, *J* 8.5, CH_2Si), 1.56 (3 H, s, MeC=C), 0.92 (6 H, s, Me_2C) and 0.30 (6 H, s, Me_2Si) (some

peaks for the minor isomer, assigned tentatively as *Z*) 5.31 (1 H, br t, *J* 8.4, C*H*=C), 2.10 (1 H, d, *J* 2.6, $CH_2C{\equiv}C$), 1.67 (2 H, d, *J* 8.5, CH_2Si), 1.75 (3 H, s, MeC=C), 0.97 (6 H, s, Me_2C) and 0.26 (6 H, s, Me_2Si).

(1*E*,6*E*)- and (1*E*,6*Z*)-1,8-Bis[dimethyl(phenyl)silyl]-4,4-dimethylocta-1,6-diene 11. Compounds (1*E*,6*E*)-**11** and (1*E*,6*Z*)-**11** (51%, 2:1 or 1:2) were prepared from the acetate **1h** (1.0 mmol) by Method A together with starting acetate (14%), (68%, 1.4:1 or 1:1.4) from the acetate **1h** (1.05 mmol) by Method A, but using 2 equivalents of the silyl-cuprate, and (47%, 1.2:1 or 1:1.2) from the acetate **1h** (1.03 mmol) by Method B; R_f (hexane) 0.30; ν_{max}(film)/cm^{-1} 1610 (C=C), 1245 (SiMe), 1115 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) (major isomer) 7.54–7.47 (2 H, m, *o*-SiArH), 7.35–7.32 (3 H, m, *p*- and *m*-SiArH), 6.09 (1 H, dt, *J* 18.4 and 7.1, CH=CSi), 5.73 (1 H, d, *J* 18.5, C=CHSi), 5.32 (2 H, m, C*H*=C*H*CH_2Si), 1.98 (2 H, dd, *J* 1.0 and 7.0, CH_2C=CSi), 1.83 (2 H, m, CH_2C=CCH_2Si), 1.68 (2 H, br d, *J* 7.2, CH_2Si), 0.79 (6 H, s, Me_2C), 0.32 (6 H, s, Me_2Si_A) and 0.26 (3 H, s, Me_2Si_B) (some peaks for the minor isomer) 6.10 (1 H, dt, *J* 18.4 and 7.0, CH=CSi), 5.74 (1 H, d, *J* 18.5, C=CHSi), 2.03 (2 H, dd, *J* 1.1 and 7.0, CH_2C=CSi), 0.84 (6 H, s, Me_2C) and 0.36 (6 H, s, Me_2Si) (Found: C, 76.7; H, 9.55. $C_{26}H_{38}Si_2$ requires C, 76.75; H, 9.4%).

(*E*)- and (*Z*)-8-[Dimethyl(phenyl)silyl]-4,4-dimethyloct-6-en-1-yne 12. Compounds (*E*)-**12** and (*Z*)-**12** (20%, 2.7:1 or 1:2.7) were prepared by Method B, (72%, 2:1 or 1:2) together with starting acetate (10%) by Method C; R_f (hexane) 0.30; ν_{max}(film)/cm^{-1} 3300 (≡CH), 2120 (C≡C), 1245 (SiMe), 1110 (SiPh) and 835 (SiMe); δ_H(250 MHz; $CDCl_3$) (major isomer) 7.55–7.49 (2 H, m, *o*-SiArH), 7.36–7.30 (3 H, m, *p*- and *m*-SiArH), 5.48 (1 H, m, C=C*H*CH_2Si), 5.30 (1 H, m, C*H*=$CHCH_2Si$), 2.03 (2 H, d, *J* 2.6, $CH_2C{\equiv}C$), 1.96 (3 H, m, HC≡C and Me_2CCH_2C=C), 1.71 (2 H, m, CH_2Si), 0.94 (6 H, s, Me_2C) and 0.28 (6 H, s, Me_2Si) (one peak for the minor isomer) 0.89 (6 H, s, Me_2C) (Found: C, 79.85; H, 9.65. $C_{18}H_{26}Si$ requires C, 79.95; H, 9.7%).

7-[Dimethyl(phenyl)silyl]-5,5-dimethylocta-1,7-dien-3-yl acetate. This compound (9%) was prepared by Method A and (5%) by Method B; R_f (EtOAc–hexane,1:9) 0.40; ν_{max}(film)/cm^{-1} 1740 (C=O), 1240 (SiMe), 1105 (SiPh) and 815 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.51–7.47 (2 H, m, *o*-SiArH), 7.34–7.30 (3 H, m, *p*- and *m*-SiArH), 5.78 (1 H, d, *J* 2.8, C$H_A$$H_B$=CSi), 5.66 (1 H, ddd, *J* 6.2, 10.4 and 17.0, C*H*=CH_2), 5.64 (1 H, d, *J* 2.9, CH_A-H_B=CSi), 5.33 (1 H, m, C*H*OAc), 5.12 (1 H, dt, *J* 17.2 and 1.2, C$H_A$$H_B$=CH), 5.05 (1 H, dt, *J* 10.4 and 1.1, $CH_A$$H_B$=CH), 2.09 (2 H, s, CH_2C=C), 1.99 (3 H, s, $MeCO_2$), 1.58 (1 H, dd, *J* 8.6 and 14.8, C$H_A$$H_B$COAc), 1.39 (1 H, dd, *J* 3.5 and 14.8, $CH_A$$H_B$-COAc), 0.80 (6 H, s, Me_2C) and 0.36 (6 H, s, Me_2Si) (Found: C, 72.95; H, 9.15. $C_{20}H_{30}O_2Si$ requires C, 72.65; H, 9.15%).

Methyl (*E*)-2-[dimethyl(phenyl)silyl]methylidene-4,4-dimethylcyclopentylmethanecarboxylate 4i. Compound **4i** (30%) together with starting ester (50%) was prepared from the ester **1i** (0.62 mmol) using the 1:1 silyl–copper reagent by Method B; R_f (EtOAc–hexane, 1:9) 0.40; ν_{max}(film)/cm^{-1} 1730 (C=O), 1615 (C=C), 1245 (SiMe), 1165 (C–O), 1110 (SiPh) and 830 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.55–7.51 (2 H, m, *o*-SiArH), 7.34–7.32 (3 H, m, *p*- and *m*-SiArH), 5.55 (1 H, br s, C=CHSi), 3.58 (3 H, s, MeO), 2.85 (1 H, m, C*H*CH_2CO_2Me), 2.41 (1 H, br d, *J* 15.5, C$H_A$$H_B$$CO_2Me$), 2.40 (1 H, m, C$H_A$$H_B$C=C), 2.15 (1 H, dd, *J* 11.5 and 15.5, $CH_A$$H_B$$CO_2Me$), 2.00 (1 H, br d, *J* 14.6, $CH_A$$H_B$C=C), 1.79 (1 H, ddd, *J* 1.9, 8.2 and 12.8, C$H_A$$H_B$CH-$CO_2Me$), 1.25 (1 H, m, $CH_A$$H_B$$CHCO_2Me$), 1.10 (3 H, s, $Me_A$$Me_B$C), 0.87 (3 H, s, $Me_A$$Me_B$C), 0.39 (3 H, s, $Me_A$$Me_B$Si) and 0.37 (3 H, s, $Me_A$$Me_B$Si) (Found: C, 71.95; H, 8.8; M^+ (CI), 316.1881. $C_{19}H_{28}O_2Si$ requires C, 72.1; H, 8.9%; *M*, 316.1858). The ester **4i** decomposed on standing in contact with silica gel to give, probably, methyl 2-[dimethyl(phenyl)silyl]methyl-4,4-dimethylcyclopent-1-enylmethanecarboxylate and methyl 2-[dimethyl(phenyl)silyl]methyl-4,4-dimethylcyclopent-2-enyl-methanecarboxylate. The vinylic signal in the ^{1}H-NMR spectrum shifts from δ 5.55 to δ 5.00 and is reduced in intensity. To avoid this rearrangement during the purification, silica gel impregnated with ammonia was used. Several other runs were carried out using different silyl-cuprate reagents, stoichiometries, and protocols, but this was the highest yield obtained.

Methyl 3-[dimethyl(phenyl)silyl]-5,5-dimethyloct-7-ynoate 15 and tentatively methyl (*E*)-7-[dimethyl(phenyl)silyl]-5,5-dimethylocta-2,7-dienoate. These compounds (7%, 3:1) were prepared using the 1:1 silyl–copper reagent by Method B; R_f (EtOAc–hexane, 1:9) 0.36; ν_{max}(film)/cm^{-1} 3350 (≡CH), 2180 and 2110 (C≡C), 1725 (C=O), 1650 (C=C), 1251 (SiMe), 1200 (C–O), 1110 (SiPh) and 820 (SiMe); δ_H(250 MHz; $CDCl_3$) (major isomer **15**) 7.52–7.46 (2 H, m, *o*-SiArH), 7.34–7.29 (3 H, m, *p*- and *m*-SiArH), 3.48 (3 H, s, MeO), 2.41 (2 H, br d, *J* 6.2, CH_2CO_2Me), 1.98 (3 H, m, C$H_2C{\equiv}CH$), 1.50 (1 H, dd, *J* 1.7 and 14.4, $Me_2CCH_AH_BCSi$), 1.40 (1 H, m, CHSi), 1.19 (1 H, dd, *J* 8.1 and 14.4, $Me_2CCH_AH_BCSi$), 0.88 (3 H, s, $Me_A$$Me_B$C), 0.86 (3 H, s, $Me_A$$Me_B$C) and 0.27 (6 H, s, Me_2Si) (some suggestive signals for the minor isomer) 7.52–7.46 (2 H, m, *o*-SiArH), 7.34–7.29 (3 H, m, *p*- and *m*-SiArH), 6.93 (1 H, dt, *J* 15.5 and 7.8, C*H*=$CHCO_2Me$), 5.78 (1 H, d, *J* 2.7, C$H_A$$H_B$=CSi), 5.71 (1 H, d, *J* 15.5, CH=C*H*CO_2Me), 5.64 (1 H, d *J* 2.8, $CH_A$$H_B$=CSi), 3.71 (3 H, s, MeO), 2.06 (4 H, m, CH_2C=CCO_2Me and CH_2CSi=C), 0.79 (6 H, s, Me_2C) and 0.35 (6 H, s, Me_2Si) (Found: C, 72.1; H, 8.85. $C_{19}H_{28}O_2Si$ requires C, 72.1; H, 8.9%).

Methyl (*E*)-3,8-bis[dimethyl(phenyl)silyl]-5,5-dimethyloct-7-enoate 13 and methyl 3,7-bis[dimethyl(phenyl)silyl]-5,5-dimethyloct-7-enoate 14. Compounds **13** and **14** (65%, 2.2:1) were prepared from the ester **1i** (1.32 mmol) by Method A using 2 equivalents of the silyl-cuprate; R_f (EtOAc–hexane, 1:9) 0.40; ν_{max}(film)/cm^{-1} 1730 (C=O), 1615 (C=C), 1250 (SiMe), 1110 (SiPh), 829 and 815 (SiMe); δ_H(250 MHz; $CDCl_3$) **13** 7.54–7.46 (2 H, m, *o*-SiArH), 7.38–7.30 (3 H, m, *p*- and *m*-SiArH), 6.05 (1 H, dt, *J* 18.4 and 7.0, CH=CSi), 5.73 (1 H, d, *J* 18.4, C=CHSi), 3.48 (3 H, s, MeO), 2.36 (2 H, m, CH_2CO_2Me), 1.99 (2 H, dd, *J* 1.3 and 7.0, CH_2C=CSi), 1.44 (2 H, m, Me_2CCH_2-CSi), 1.02 (1 H, m, CHSi), 0.81 (3 H, s, $Me_A$$Me_B$C), 0.75 (3 H, s, $Me_A$$Me_B$C), 0.31 (6 H, s, Me_2Si_A) and 0.26 (6 H, s, Me_2Si_B) (some signals for **14**) 5.72 (1 H, d, *J* 2.9, C$H_A$$H_B$=CSi), 5.59 (1 H, d, *J* 2.9, $CH_A$$H_B$=CSi), 3.46 (3 H, s, MeO), 0.71 (3 H, s, $Me_A$$Me_B$C) and 0.66 (3 H, s, $Me_A$$Me_B$C).

(*E*)-1-[Dimethyl(phenyl)silyl]methylidene-4,4-dimethyl-2-methylidenecyclopentane 4j. Compound **4j** (16%) was prepared from the bisacetylene **1j** (0.83 mmol) by Method B, (34%) from the bisacetylene **1j** (0.41 mmol) by Method C; R_f (hexane) 0.40; ν_{max}(film)/cm^{-1} 1248 (SiMe), 1112 (SiPh) and 834 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.58–7.49 (2 H, m, *o*-SiArH), 7.35–7.31 (3 H, m, *p*- and *m*-SiArH), 5.59 (1 H, br s, C=CHSi), 5.08 (1 H, t, *J* 2.0, C$H_A$$H_B$=C), 4.84 (1 H, br s, $CH_A$$H_B$=C), 2.35 (2 H, d, *J* 1.5, CH_2C=CH_2), 2.22 (2 H, s, CH_2C=CHSi), 1.00 (6 H, s, Me_2C) and 0.37 (6 H, s, Me_2Si). The cyclopentane is sensitive to acid, giving at least two compounds (^{1}H-NMR) on standing in deuterated chloroform for 2 d.

(1*E*,6*E*)-1,7-Bis[dimethyl(phenyl)silyl]-4,4-dimethylhepta-1,6-diene 16. Compound **16** (43%) was prepared by Method B; R_f (hexane) 0.28; ν_{max}(film)/cm^{-1} 1614 (C=C), 1247 (SiMe), 1113 (SiPh) and 837 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.56–7.48 (2 H, m, *o*-SiArH), 7.37–7.31 (3 H, m, *p*- and *m*-SiArH), 6.14 (1 H, dt, *J* 7.0 and 18.5, CH=CSi), 5.78 (1 H, d, *J* 18.4, C=CHSi), 2.07 (2 H, dd, *J* 0.8 and 7.0, CH_2C=C), 0.90 (3 H, s, Me_2C) and 0.34 (3 H, s, Me_2Si).

(*Z*)-2-[Dimethyl(phenyl)silyl]methylidene-1-methylcyclopentanol 18. Compound **18** (11%) was prepared from the ketone **17**[24] (2.6 mmol) by Method A, (28%) from the ketone **17** (1.8 mmol) by Method B; R_f (EtOAc–hexane, 1:9) 0.35; ν_{max}(film)/cm^{-1} 3572 and 3460 (OH), 1628 (C=C), 1246 (SiMe), 1110 (SiPh) and 828 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.61–7.54 (2 H, m, *o*-SiArH), 7.39–7.30 (3 H, m, *p*- and *m*-SiArH), 5.52 (1 H, t, *J* 2.1, C=CHSi), 2.50 (2 H, m, CH_2C=C), 1.64 (4 H, m, CH_2-CH_2COH), 1.21 (3 H, s, *Me*COH), 0.47 (3 H, s, Me_AMe_BSi) and 0.38 (3 H, s, $Me_A Me_B Si$), and a byproduct, tentatively assigned as the *E*-isomer of **18**, (9%) by Method B; R_f (EtOAc–hexane, 1:9) 0.37; ν_{max}(film)/cm^{-1} 3510 (OH), 1630 (C=C), 1245 (SiMe), 1118 (SiPh) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.59–7.49 (2 H, m, *o*-SiArH), 7.40–7.33 (3 H, m, *p*- and *m*-SiArH), 5.18 (1 H, t, *J* 2.1, C=CHSi), 3.61 (1 H, br s, OH), 2.47 (2 H, m, CH_2C=C), 1.79 (4 H, m, CH_2CH_2COH), 1.35 (3 H, s, *Me*COH) and 0.43 (6 H, s, Me_2Si).

(*E*)-7-[Dimethyl(phenyl)silyl]hept-6-en-2-one 19. Compound **19** (55%) was prepared from the ketone **17**[24] by Method A, (33%) Method B; R_f (EtOAc–hexane, 1:9) 0.30; ν_{max}(film)/cm^{-1} 1716 (C=O), 1616 (C=C), 1248 (SiMe), 1112 (SiPh), 842 and 824 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.52–7.47 (2 H, m, *o*-SiArH), 7.37–7.32 (3 H, m, *p*- and *m*-SiArH), 6.05 (1 H, dt, *J* 18.6 and 6.1, CH=CSi), 5.77 (1 H, dt, *J* 18.6 and 1.3, C=CHSi), 2.42 (2 H, t, *J* 7.4, CH_2CO), 2.11 (5 H, m, MeCO and CH_2C=CSi), 1.69 (2 H, quintet, *J* 7.4, CH_2CH_2CO) and 0.31 (6 H, s, Me_2Si) (Found: C, 72.95; H, 8.8. $C_{15}H_{22}OSi$ requires C, 73.1; H, 9.0%).

(*E*)-1,7-Bis[dimethyl(phenyl)silyl]-4,4-dimethylhept-6-en-1-yne 24. Compound **24** (14%) was prepared from the acetylene **23** (0.41 mmol) by Method B; R_f (hexane) 0.20; ν_{max}(film)/cm^{-1} 2173 (C≡C), 1613 (C=C), 1249 (SiMe), 1114 (SiPh) and 837 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.66–7.61 (2 H, m, *o*-Si_AArH), 7.54–7.49 (2 H, m, *o*-Si_BArH), 7.37–7.33 (6 H, m, *p*- and *m*- Si_AArH and *p*- and *m*-Si_BArH), 6.11 (1 H, dt, *J* 18.4 and 7.0, CH=CSi), 5.83 (1 H, d, *J* 18.4, C=CHSi), 2.18 (2 H, d, *J* 7.0, CH_2C=C), 2.15 (2 H, s, CH_2C≡C), 0.99 (6 H, s, Me_2C), 0.40 (6 H, s, Me_2Si_A) and 0.33 (6 H, s, Me_2Si_B).

2-[Dimethyl(phenyl)silyl]-4,4-dimethyl-7-trimethylsilylhept-6-yn-2-ol 26. Compound **26** (25%) was prepared together with the starting ketone (50%) from the ketone **25** (0.74 mmol) to which boron trifluoride–ether complex (0.85 mmol) had been added before addition of the silyl-cuprate by Method A; R_f (EtOAc–hexane, 1:9) 0.34; ν_{max}(film)/cm^{-1} 3550 and 3490 (OH), 2160 (C≡C), 1710 (C=O), 1245 (SiMe) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.59–7.53 (2 H, m, *o*-SiArH), 7.37–7.33 (3 H, m, *p*- and *m*-SiArH), 2.35 (1 H, d, *J* 16.7, CH_AH$_B$C≡C), 2.21 (1 H, d, *J* 16.7, CH$_A$$H_B$C≡C), 1.77 (1 H, d, *J* 15.1, CH_AH$_B$COH), 1.50 (1 H, d, *J* 15.1, CH$_A$$H_B$COH), 1.36 (3 H, s, *Me*COH), 1.07 (3 H, s, Me_AMe_BC), 1.04 (3 H, s, $Me_A Me_B C$), 0.33 (6 H, s, Me_2SiPh) and 0.13 (6 H, s, Me_3Si) (Found: C, 69.15; H, 9.75. $C_{20}H_{34}OSi_2$ requires C, 69.3; H, 9.9%). This compound was also prepared from the ketone **25** (0.55 mmol) and dimethyl(phenyl)silyllithium (0.65 mmol).

(*E*)- and (*Z*)-4,4,6-Trimethylnon-6-en-1-yne

Allylic acetate **1g** (1.6 mmol) was treated with lithium dimethylcuprate made from methyllithium (4 mmol) and copper(I) iodide (2 mmol) in the same way as Method A. Short column chromatography (SiO_2, pentane) gave a mixture of the *alkenes* (85%, 3:1 or 1:3); R_f (EtOAc–hexane, 15:85) 0.74; ν_{max}(film)/cm^{-1} 3310 (≡CH) and 2130 (C≡C); δ_H(250 MHz; $CDCl_3$) (major) 5.15 (1 H, t, *J* 7.0 CH=C), 2.05 (2 H, d, *J* 2.8, CH_2C≡C), 1.99 (5 H, m, Me_2CCH_2C=C, MeCH_2C=C and HC≡C), 1.65 (3 H, s, MeC=C), 0.95 (6 H, s, Me_2C) and 0.94 (3 H, t, *J* 7.1, *Me*CH_2C=C) (identifiable peaks for the minor) 5.25 (1 H, t, *J* 7.1 CH=C), 2.09 (2 H, d, *J* 2.6, CH_2C≡C), 1.75 (3 H, s, MeC=C), 0.99 (6 H, s, Me_2C) and 0.91 (3 H, t, *J* 7.0, *Me*CH_2C=C) (Found: C, 87.6; H, 12.05. $C_{12}H_{20}$ requires C, 87.75; H, 12.25%). There was no trace of these products from the reaction of the mixed cuprate on **1g** in Method C.

2-[Dimethyl(phenyl)silyl]-4,4-dimethylocta-1,7-diene

Hydrochloric acid (12 mol dm^{-3} in water, 0.3 cm^3), water (0.3 cm^3), methanol (0.3 cm^3) and the crude allyl- and vinylsilane **11** (0.15 g, 0.37 mmol) in THF (2 cm^3) were refluxed for 5 d. Water (15 cm^3) was added and the mixture extracted with ether (3 × 10 cm^3). The organic extracts were combined, washed with saturated sodium hydrogen carbonate solution (3 × 10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, hexane) to give the *vinylsilane* (0.016 g, 16%); R_f (hexane) 0.37; ν_{max}(film)/cm^{-1} 1640 (C=C), 1250 (SiMe), 1110 (SiPh) and 820 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.54–7.47 (2 H, m, *o*-SiArH), 7.36–7.31 (3 H, m, *p*- and *m*-SiArH), 5.76 (1 H, d, *J* 2.8, CH_AH$_B$=CSi), 5.75 (1 H, ddt, *J* 17.1, 6.5 and 10.1, CH_2CH=CH_2), 5.60 (1 H, d, *J* 2.9, CH$_A$$H_B$=CSi), 4.93 (1 H, ddd, *J* 1.6, 3.5 and 17.1, CH_AH$_B$=CH), 4.88 (1 H, ddt, *J* 10.2, 2.2 and 1.2, CH$_A$$H_B$=CH), 2.07 (2 H, d, *J* 0.7, Me_2-CCH_2C=C), 1.95 (2 H, tq, *J* 1.3 and 8.1, CH_2CH=CH_2), 1.22 (2 H, m, $Me_2CCH_2CH_2$), 0.77 (6 H, s, Me_2C) and 0.37 (6 H, s, Me_2Si) (Found: M$^+$, 272.1961. $C_{18}H_{28}Si$ requires *M*, 272.1960).This relatively involatile product must have come from the protodesilylation of the regioisomeric vinylsilane accompanying the substrate.

Starting materials

2-(2,2-Dimethylpent-4-ynyl)-2-methyloxirane 1e. Following Matteson,[25] *n*-butyllithium (1.6 mol dm^{-3} in hexane, 5 cm^3) was added dropwise over 15 min to a well stirred solution of 4,4-dimethylhept-6-yn-2-one[25] (1.0 g, 7.2 mmol) and dibromomethane (2.06 g, 11.9 mmol) in dry THF (15 cm^3) under argon at −78 °C, and at room temperature overnight. The mixture was quenched with saturated ammonium chloride solution (10 cm^3) and extracted with ether (3 × 10 cm^3). The organic extracts were combined, dried ($MgSO_4$) and evaporated by careful fractional distillation. The residue was distilled to give the *epoxide* (0.82 g, 75%), bp 63–68 °C/8 mmHg; R_f (EtOAc–hexane,1:9) 0.32; ν_{max}(film)/cm^{-1} 3300 (≡CH) and 2120 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.66 (1 H, br d, *J* 4.9, CH_AH$_B$O), 2.57 (1 H, dd *J* 1.3 and 4.9, CH$_A$$H_B$O), 2.15 (2 H, d, *J* 2.6, CH_2C≡C), 2.00 (1 H, t, *J* 2.7, HC≡C), 1.80 (1 H, dd, *J* 1.3 and 14.2, CH_AH$_B$CO), 1.44 (1 H, br d, *J* 14.3, CH$_A$$H_B$CO), 1.39 (3 H, s, MeCO) and 1.07 (6 H, s, Me_2C) (Found: C, 78.75; H, 10.85. $C_{10}H_{16}O$ requires C, 78.9; H, 10.6%). A byproduct was assigned the structure *12,13-epoxy-4,4,6,10,10,12-hexamethyltrideca-1,7-diyn-6-ol* (0.10 g, 5%); R_f (EtOAc–hexane, 1:9) 0.07; ν_{max}(film)/cm^{-1} 3450 (OH), 3300 (≡CH) and 2120 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.64 (1 H, br d, *J* 4.9, CH_AH$_B$O), 2.57 (1 H, dd *J* 1.9 and 4.2, CH$_A$$H_B$O), 2.33 (2 H, d, *J* 2.5, CH_2C=CH), 2.16 (2 H, s, CH_2C≡CC(Me)OH), 2.00 (1 H, t, *J* 2.6, HC≡C), 1.95 (1 H, br s, OH), 1.78 (1 H, dd, *J* 1.2 and 14.9, CH_AH$_B$COC), 1.75 (2 H, s, CH_2COH), 1.51 (3 H, s, *Me*COH), 1.40 (1 H, masked d, CH$_A$$H_B$COC), 1.38 (3 H, s, MeCOC), 1.17 (3 H, s, $Me_AMe_BCCH_2COH$), 1.15 (3 H, s, $Me_A Me_B CCH_2COH$), 1.05 (3 H, s, $Me_AMe_BCCH_2COC$) and 1.04 (3 H, s, $Me_A Me_B CCH_2COC$) (Found: C, 78.4; H, 10.35. $C_{19}H_{30}O_2$ requires C, 78.55; H, 10.4%).

3,5,5-Trimethyloct-1-en-7-yn-3-ol. Following Johnson,[26] the ketone **1b** (1.80 g, 13.0 mmol) in dry THF (12 cm^3) was added dropwise to a stirred solution of vinylmagnesium bromide (1.0 mol dm^{-3} in THF; 18 cm^3) in dry THF (25 cm^3) under argon at 0 °C. The red–brown solution became clear yellow, the cooling bath was removed, the solution stirred at room temperature for 2 h, then cooled to 0 °C, quenched with saturated ammonium chloride solution (50 cm^3) and extracted with ether (3 × 50 cm^3). The organic extracts were combined, washed with water

until neutral (4 × 80 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The *alcohol* (2.07 g, 96%) was used in the next reaction without further purification; R_f (EtOAc–hexane, 15 : 85) 0.34; ν_{max}(film)/cm^{-1} 3460 (OH), 3300 (≡CH) and 2120 (C≡C); δ_H(250 MHz; $CDCl_3$) 6.00 (1 H, dd, *J* 10.7 and 17.3, C*H*=CH_2), 5.22 (1 H, dd, *J* 1.2 and 17.3, CH_AH_B=C), 5.00 (1 H, dd, *J* 1.2 and 10.7, CH_AH_B=C), 2.21 (2 H, d, *J* 2.6, CH_2C≡C), 2.01 (1 H, t, *J* 2.7, HC≡C), 1.70 (2 H, s, CH_2COH), 1.63 (1 H, s, OH), 1.27 (3 H, s, *Me*COH) and 1.04 (6 H, s, Me_2C) (Found: C, 79.55; H, 10.85. $C_{11}H_{18}O$ requires C, 79.45; H, 10.9%).

3,5,5-Trimethyloct-1-en-7-yn-3-yl acetate 1g. Following Höfle and Steglich,[23] acetic anhydride (0.80 g, 0.74 cm^3, 7.8 mmol) was added dropwise to a stirred solution of the alcohol (1.00 g, 6.0 mmol) and 4-dimethylaminopyridine (0.88 g, 7.2 mmol) in dry dichloromethane (5 cm^3) under argon at 0 °C. The solution was kept for 24 h at room temperature, more acetic anhydride (0.80 g, 7.8 mmol, 0.74 cm^3) was added and stirring continued for 40 h. Water (5 cm^3) was added, dichloromethane evaporated under reduced pressure and the residue extracted with ether (4 × 20 cm^3). The organic extracts were combined, washed with hydrochloric acid (1.5 mol dm^{-3} in water, 4 × 10 cm^3) and saturated sodium hydrogen carbonate solution (3 × 15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 4 : 96) to give the *acetate* (0.69 g, 55%); R_f (EtOAc–hexane, 15 : 85) 0.49; ν_{max}(film)/cm^{-1} 3310 (≡CH), 2115 (C≡C), 1740 (C=O) and 1645 (C=C); δ_H(250 MHz; $CDCl_3$) 5.99 (1 H, dd, *J* 11.0 and 17.4, C*H*=CH_2), 5.18 (1 H, dd, *J* 0.8 and 17.4, CH_AH_B=C), 5.05 (1 H, dd, *J* 0.7 and 11.0, CH_AH_B=C), 2.21 (1 H, dd, *J* 2.6 and 16.6, CH_AH_BC≡C), 2.18 (1 H, d, *J* 15.2, CH_AH_BCOAc), 2.13 (1 H, dd, *J* 2.5 and 16.6, CH_AH_BC≡C), 2.01 (3 H, s, $MeCO_2$), 1.99 (1 H, t, *J* 2.6, HC≡C), 1.76 (1 H, d, *J* 15.1, CH_AH_BCOAc), 1.59 (3 H, s, *Me*COAc) and 1.04 (6 H, s, Me_2C) (Found: C, 74.95; H, 9.8. $C_{13}H_{20}O_2$ requires C, 74.95; H, 9.7%).

7-[Dimethyl(phenyl)silyl]-4,4-dimethylhept-6-yn-2-one. Following Marshall[27] and Corey,[28] chlorodimethyl(phenyl)silane[29] (5.97 g, 5.3 cm^3, 35.0 mmol) was added dropwise with stirring to diisopropylamine (3.34 g, 33.0 mmol, 4.6 cm^3) and *n*-butyllithium (1.5 mol dm^{-3} in hexane, 21.3 cm^3) in dry THF (50 cm^3) under argon at −78 °C. After 10 min, the ketone **1b** (2.0 g, 14.5 mmol) in dry THF (10 cm^3) was added at −78 °C, stirred for 1 h at −78 °C, allowed to warm to room temperature and quenched by stirring overnight with dilute sulfuric acid (1.8 mol dm^3 in water, 50 cm^3). The mixture was extracted with ether (3 × 40 cm^3), the organic extracts were combined, washed with water (3 × 30 cm^3) and saturated sodium hydrogen carbonate solution until neutral (3 × 40 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 7 : 93) to give the *ketone* (3.83 g, 97%); R_f (EtOAc–hexane,1 : 9) 0.35; ν_{max}(film)/cm^{-1} 2172 (C≡C), 1716 (C=O), 1249 (SiMe), 1115 (SiPh) and 817 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.62–7.57 (2 H, m, *o*-SiArH), 7.35–7.31 (3 H, m, *p*- and *m*-SiArH), 2.44 (2 H, s, CH_2CO), 2.30 (2 H, s, CH_2C≡C), 1.06 (6 H, s, Me_2C) and 0.36 (6 H, s, Me_2Si) (Found: M^+, 272.1608. $C_{17}H_{24}OSi$ requires *M*, 272.1596).

1-[Dimethyl(phenyl)silyl]-4,4-dimethylhepta-1,6-diyne 23. Following Negishi,[30] diisopropylamine (1.02 g, 1.42 cm^3, 10.1 mmol) and *n*-butyllithium (1.35 mol dm^{-3} in hexane, 7.5 cm^3) in dry THF (15 cm^3) under argon at 0 °C was stirred for 30 min, then cooled to −78 °C and the ketone (2.6 g, 9.6 mmol) in dry THF (10 cm^3) was added. After 15 min diethyl chlorophosphate (1.74 g, 1.5 cm^3, 10.1 mmol) was added dropwise, and the solution stirred at room temperature for 2.5 h, then cooled again to −78 °C and transferred by cannula over 0.5 h to a stirred solution of diisopropylamine (2.23 g, 22.0 mmol, 3.1 cm^3) and *n*-butyllithium (1.35 mol dm^{-3} in hexane, 15.4 cm^3) in dry THF (25 cm^3) under argon at −78 °C. The mixture was allowed to warm to room temperature overnight, cooled to 0 °C, quenched with water (25 cm^3) and extracted with ether (3 × 25 cm^3). The organic extracts were combined, washed with cold hydrochloric acid (1 mol dm^{-3} in water, 30 cm^3), water (3 × 25 cm^3) and saturated sodium hydrogen carbonate solution until neutral (3 × 30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1 : 99) to give the *acetylene* (1.79 g, 73%); R_f (hexane) 0.24; ν_{max}(film)/cm^{-1} 3308 (≡CH), 2174 and 2117 (C≡C), 1249 (SiMe), 1115 (SiPh) and 817 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.66–7.60 (2 H, m, *o*-SiArH), 7.39–7.34 (3 H, m, *p*- and *m*-SiArH), 2.29 (2 H, s, CH_2C≡CSi), 2.21 (2 H, d, *J* 2.65, CH_2C≡CH), 2.01 (1 H, t, *J* 2.65, CH_2C≡C*H*), 1.08 (6 H, s, Me_2C) and 0.39 (6 H, s, Me_2Si) (Found: M^+, 254.1500. $C_{17}H_{22}Si$ requires *M*, 254.1491) (Found: C, 80.25; H, 8.9. $C_{17}H_{22}Si$ requires C, 80.25; H, 8.7%). We assigned the structure *7-[dimethyl(phenyl)silyl]-4,4-dimethylnona-5,6-dien-1-yne* to a byproduct (6–7%) in some runs of this reaction; R_f (hexane) 0.30; ν_{max}(film)/cm^{-1} 3311 (≡CH), 2118 (C≡C), 1932 (C=C=C), 1253 (SiMe), 1119 (SiPh) and 832 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.57–7.48 (2 H, m, *o*-SiArH), 7.40–7.30 (3 H, m, *p*- and *m*-SiArH), 4.99 (1 H, t, *J* 3.3, CH=C=C), 2.11 (2 H, d, *J* 2.6, CH_2C≡CH), 1.95 (1 H, t, *J* 2.6, HC≡C), 1.89 (2 H, dq, *J* 3.3 and 7.3, C$H_2$$CH_3$), 1.08 (3 H, s, *Me*$_AMe_B$C), 1.07 (3 H, s, Me$_A$-*Me*$_B$C), 0.98 (3 H, t, *J* 7.3, CH_2CH_3), 0.36 (3 H, s, *Me*$_A$Me$_B$Si) and 0.32 (3 H, s, Me$_A$*Me*$_B$Si) (Found: M^+, 282.1783. $C_{19}H_{26}Si$ requires *M*, 282.1804).

4,4-Dimethylhepta-1,6-diyne 1j. Following Marshall,[31] tetra-*n*-butylammonium fluoride (1.0 mol dm^{-3} in THF, 4.3 cm^3) was added dropwise with stirring to the silylacetylene (1.05 g, 4.1 mmol) in dry THF (4 cm^3) under argon at 0 °C. After 0.5 h, water (20 cm^3) was added and the mixture extracted with ether (3 × 10 cm^3). The organic extracts were combined, washed with water (3 × 20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure without heating. The residue was distilled (Kugelrohr, 65–70 °C/20 mmHg) to give the *acetylene* (0.42 g, 85%); R_f (EtOAc–hexane, 1 : 9) 0.12; ν_{max}(film)/cm^{-1} 3303 (≡CH) and 2117 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.19 (2 H, d, *J* 2.65, CH_2C≡C), 2.00 (1 H, t, *J* 2.65, HC≡C), 1.06 (3 H, s, Me_2C) (Found: M^+, 120.0929. C_9H_{12} requires *M*, 120.0939).

4,4-Dimethyl-2-trimethylsilyl-7-trimethylsilyloxyhept-6-en-1-yne 27. Following Marshall[27] and Corey,[28] chlorotrimethylsilane (5.98 g, 7.0 cm^3, 55 mmol) and the ketone **1b** (3.04 g, 22.0 mmol) in dry THF (10 cm^3) were added sequentially dropwise with stirring to diisopropylamine (5.26 g, 52 mmol, 7.29 cm^3) and *n*-butyllithium (1.52 mol dm^{-3} in hexane, 33 cm^3) in dry THF (75 cm^3) under argon at −78 °C, the mixture was stirred at that temperature for 2 h, quenched with water (20 cm^3) and extracted with ether (3 × 30 cm^3). The organic extracts were combined, washed with cold hydrochloric acid (1 mol dm^{-3}, 30 cm^3), saturated sodium hydrogen carbonate solution (3 × 30 cm^3) and water (3 × 25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the *silyl enol ether* (6.08 g, 98%); R_f (EtOAc–hexane, 1 : 9) 0.65; ν_{max}(film)/cm^{-1} 2180 (C≡C), 1620 (C=C), 1250 (SiMe), 1030 (C–O) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 4.07 (1 H, s, CH_AH_B=C), 4.03 (1 H, s, CH_AH_B=C), 2.17 (2 H, s, CH_2C≡C), 2.01 (2 H, s, CH_2C=C), 0.99 (6 H, s, Me_2C), 0.20 (9 H, s, Me_3SiO) and 0.14 (9 H, s, Me_3Si) (Found: C, 63.65; H, 10.6. $C_{15}H_{30}OSi_2$ requires C, 63.75; H, 10.7%).

4,4-Dimethyl-7-trimethylsilylhept-6-yn-2-one 25. This was prepared in the same way as the enol ether **27** above, but the reaction was quenched with sulfuric acid (1 mol dm^{-3} in water, 100 cm^3) and stirred overnight. Workup and chromatography (SiO_2, EtOAc–hexane, 7 : 93) gave the *ketone* (4.2 g, 91%); R_f (EtOAc–hexane,1 : 9) 0.34; ν_{max}(film)/cm^{-1} 2180 (C≡C), 1720 (C=O), 1250 (SiMe) and 845 (SiMe); δ_H(250 MHz; $CDCl_3$) 2.45 (2 H, s, CH_2C=O), 2.25 (2 H, s, CH_2C≡C), 2.13 (3 H, s,

MeC=O), 1.06 (6 H, s, Me_2C) and 0.14 (9 H, s, Me_3Si) (Found: C, 68.3; H, 10.6. $C_{12}H_{22}OSi$ requires C, 68.5; H, 10.55%).

1-Hydroxy-4,4-dimethyl-7-trimethylsilylhept-6-yn-2-one. Following Rubottom,[32] *m*-chloroperbenzoic acid (80% purity, 3.65 g, 17 mmol) was added in 10 portions over 15 min with stirring to the enol ether **27** (3.82 g, 13.6 mmol) in dry dichloromethane (20 cm^3) under argon at 0 °C. The white suspension was stirred at room temperature for 10 min, hydrochloric acid (1.5 mol dm^{-3} in water, 20 cm^3) was added, and the mixture stirred at room temperature overnight. The mixture was extracted with dichloromethane (3 × 35 cm^3), the organic extracts were combined, washed with saturated sodium hydrogen carbonate solution (4 × 25 cm^3) and water (2 × 25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the hydroxyketone (3.02 g, 98%), which was used in the next step. A sample was chromatographed (SiO_2, EtOAc–hexane, 15:85) to give a purer sample of the *hydroxyketone*; R_f (EtOAc–hexane, 2:8) 0.28; ν_{max}(film)/cm^{-1} 3470 (OH), 2180 (C≡C), 1720 (C=O), 1250 (SiMe) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 4.20 (2 H, s, CH_2OH), 3.15 (1 H, br s, OH), 2.41 (2 H, s, Me_2CCH_2C=O), 2.24 (2 H, s, CH_2C≡C), 1.08 (6 H, s, Me_2C) and 0.14 (9 H, s, Me_3Si) (Found: M^+, 226.1383. $C_{12}H_{22}O_2Si$ requires *M*, 226.1389).

4,4-Dimethyl-7-trimethylsilylhept-6-yne-1,2-diol 28. Sodium borohydride (0.27 g, 7.1 mmol) was added in 10 portions over 15 min with stirring to the hydroxyketone (3.29 g, 14.6 mmol) in methanol (40 cm^3) at 0 °C and the mixture stirred for 20 min at 0 °C. The solvent was removed under reduced pressure, water (40 cm^3) added and the mixture extracted with ether (5 × 20 cm^3). The organic extracts were combined, washed with water (40 cm^3) and brine (2 × 20 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give crude diol (3.01 g, 90%) containing a small amount of the corresponding desilylated diol. A sample was chromatographed (SiO_2, EtOAc–hexane, 1:1) to give the *diol*; R_f (EtOAc–hexane, 1:1) 0.31; ν_{max}(film)/cm^{-1} 3360 (OH), 2180 (C≡C), 1250 (SiMe) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 3.85 (1 H, tt, *J* 3.2 and 8.0, C*H*OH), 3.54 (1 H, dd, *J* 3.4 and 10.9, CH_AH_BOH), 3.39 (1 H, dd, *J* 8.1 and 10.9, CH_AH_B-OH), 2.24 (2 H, s, 2 × OH), 2.20 (2 H, s, CH_2C≡C), 1.45 (1 H, dd, *J* 7.9 and 14.8, $Me_2CCH_AH_BCHOH$), 1.37 (1 H, dd, *J* 2.9 and 14.8, $Me_2CCH_AH_BCHOH$), 1.03 (3 H, s, Me_AMe_BC), 1.02 (3 H, s, Me_AMe_BC) and 0.14 (9 H, s, Me_3Si) (Found: C, 62.8; H, 10.6. $C_{12}H_{24}O_2Si$ requires C, 63.1; H, 10.6%).

2-Hydroxy-4,4-dimethyl-7-trimethylsilylhept-6-yn-1-yl toluene-*p*-sulfonate. Toluene-*p*-sulfonyl chloride (0.21 g, 1.11 mmol) was added in 4 portions over 5 min with stirring to the diol **28** (0.21 g, 0.92 mmol) and 4-dimethylaminopyridine (0.011 g, 0.09 mmol) in dry pyridine (1 cm^3) under argon at room temperature, and stirred overnight. Water (4 cm^3) was added and the mixture extracted with ether (3 × 10 cm^3). The organic extracts were combined, washed with hydrochloric acid (1.5 mol dm^{-3} in water, 4 × 5 cm^3) and saturated sodium hydrogen carbonate solution (4 × 5 cm^3) and water (2 × 5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9 and then 15:85) to give the *tosylate* (0.28 g, 79.5%); R_f (EtOAc–hexane, 2:8) 0.25; ν_{max}(film)/cm^{-1} 3540 (OH), 2180 (C≡C), 1600 (ArH), 1450 (SiMe), 1190 and 1180 (S=O) and 840 (SiMe); δ_H(250 MHz; $CDCl_3$) 7.79 (2 H, d, *J* 8.3, *o*-SArH), 7.34 (2 H, d, *J* 8.0, *m*-SArH), 3.95 (2 H, m, C*H*OH and $CH_AH_BOSO_2$), 3.84 (1 H, dd, *J* 7.8 and 18.3, $CH_AH_BOSO_2$), 2.44 (3 H, s, MePh), 2.16 (2 H, s, CH_2C≡C), 1.44 (1 H, dd, *J* 8.2 and 14.7, Me_2CCH_A-H_BCHOH), 1.35 (1 H, dd, *J* 2.8 and 14.7, $Me_2CCH_AH_B$-CHOH), 0.99 (3 H, s, Me_AMe_BC), 0.98 (3 H, s, Me_AMe_BC) and 0.12 (9 H, s, Me_3Si).

2-(2,2-Dimethylpent-4-ynyl)oxirane 1d. Following Terashima,[33] tetra-*n*-butylammonium fluoride (1.0 mol dm^{-3} in THF, 8 cm^3) was added dropwise with stirring to the tosylate (1.22 g, 3.18 mmol) in THF (15 cm^3) under argon at room temperature. The dark green solution was stirred for 10 min, water (10 cm^3) added and the mixture extracted with ether (4 × 15 cm^3). The organic extracts were combined, washed with water (4 × 15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure without heating. The residue was chromatographed (SiO_2, Et_2O–light petroleum, 6:94) to give the *epoxide* (0.21 g, 48%) in low yield because of its volatility; R_f (EtOAc–hexane, 2:8) 0.51; ν_{max}(film)/cm^{-1} 3320 (≡CH) and 2130 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.97 (1 H, m, CH_2CHO), 2.75 (1 H, br t, *J* 4.5, CH_AH_BO), 2.45 (1 H, dd, *J* 2.7 and 5.1, CH_AH_BO), 2.20 (1 H, dd, *J* 2.6 and 16.7, CH_AH_BC≡C), 2.14 (1 H, dd, *J* 2.7 and 16.7, CH_AH_BC≡C), 2.00 (1 H, t, *J* 2.6, HC≡C), 1.58 (1 H, dd, *J* 5.1 and 14.2, CH_AH_BCHO), 1.49 (1 H, dd, *J* 6.7 and 14.2, CH_AH_BCHO) and 1.08 (6 H, s, Me_2C) (Found: C, 78.1; H, 10.1. $C_9H_{14}O$ requires C, 78.2; H, 10.2%).

3,3-Dimethylhex-5-ynal 1f. Following Marshall[31] and Roush,[34] tetra-*n*-butylammonium fluoride (1.0 mol dm^{-3} in THF, 14 cm^3) was added dropwise with stirring to the diol **28** (2.85 g, 12.5 mmol) in THF (12 cm^3) at room temperature, and the mixture stirred for 30 min at room temperature. This solution was used directly in the next step, but a sample of *4,4-dimethylhept-6-yne-1,2-diol* was characterised; R_f (EtOAc–hexane, 1:1) 0.19; ν_{max}(film)/cm^{-1} 3370 (OH), 3300 (≡CH) and 2120 (C≡C); δ_H(250 MHz; $CDCl_3$) 3.84 (1 H, tt, *J* 3.0 and 8.2, CH_2CHOH), 3.56 (1 H, dd, *J* 3.3 and 10.9, CH_AH_BOH), 3.38 (1 H, dd, *J* 8.2 and 10.9, CH_AH_BOH), 2.37 (2 H, br s, 2 × OH), 2.21 (1 H, dd, *J* 2.7 and 16.7, CH_AH_BC≡C), 2.15 (1 H, dd, *J* 2.7 and 16.7, CH_AH_BOH), 2.01 (1 H, t, *J* 2.7, HC≡C), 1.47 (1 H, dd, *J* 8.3 and 14.7, $Me_2CCH_AH_BCHOH$), 1.36 (1 H, dd, *J* 2.6 and 14.7, $Me_2CCH_AH_BCHOH$), 1.04 (3 H, s, Me_AMe_BC) and 1.03 (3 H, s, Me_AMe_BC). The solution was diluted with THF (15 cm^3) and water (40 cm^3), and then stirred under argon at room temperature with sodium periodate (3.21 g, 15.0 mmol), added in 10 portions over 15 min. After 1.5 h stirring at room temperature, water (60 cm^3) was added and the mixture extracted with ether (3 × 50 cm^3). The organic extracts were combined, washed with saturated sodium hydrogen carbonate solution (5 × 50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure without heating to give the aldehyde[35] (1.53 g, 99%). A sample was chromatographed (SiO_2, Et_2O–pentane, 8:92); R_f (EtOAc–hexane, 1:9) 0.30; ν_{max}(film)/cm^{-1} 3280 (≡CH), 2740 (CH aldehyde), 2115 (C≡C) and 1715 (C=O); δ_H(250 MHz; $CDCl_3$) 9.80 (1 H, t, *J* 2.7, HC=O), 2.42 (2 H, d, *J* 2.7, CH_2CHO), 2.22 (2 H, d, *J* 2.6, CH_2C≡C), 2.04 (1 H, t, *J* 2.6, HC≡C) and 1.13 (6 H, s, Me_2C).

3,3-Dimethylhex-5-yn-1-ol. Sodium borohydride (0.23 g, 6.1 mmol) was added in 10 portions over 15 min with stirring to the aldehyde **1f** (1.23 g, 9.9 mmol) in methanol (40 cm^3) at 0 °C. The solvent was removed under reduced pressure, water (50 cm^3) added and the mixture extracted with ether (4 × 50 cm^3). The organic extracts were combined, washed with water (2 × 50 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:1) to give the *alcohol* (0.72 g, 58%); R_f (EtOAc–hexane, 1:1) 0.38; ν_{max}(film)/cm^{-1} 3400 (OH), 3308 (≡CH) and 2115 (C≡C); δ_H(250 MHz; $CDCl_3$) 3.72 (2 H, t, *J* 7.3, CH_2OH), 2.11 (2 H, d, *J* 2,7, CH_2C≡C), 2.00 (1 H, t, *J* 2.6, HC≡C), 1.63 (2 H, t, *J* 7.3, CH_2CH_2OH), 1.24 (1 H, br s, OH) and 1.00 (6 H, s, Me_2C).

3,3-Dimethylhex-5-yn-1-yl toluene-*p*-sulfonate 1a. Toluene-*p*-sulfonyl chloride (1.14 g, 6.0 mmol) was added in 10 portions over 15 min with stirring to 3,3-dimethylhex-5-yn-1-ol (0.51 g, 4.0 mmol) and 4-dimethylaminopyridine (0.048 g, 0.4 mmol) in dry pyridine (5 cm^3) under argon at room temperature. After 15 min the mixture was quenched with water (15 cm^3) and

extracted with ether (4 × 20 cm^3). The organic extracts were combined, washed with hydrochloric acid (1.5 mol dm^{-3} in water, 4 × 25 cm^3), saturated sodium hydrogen carbonate solution (4 × 25 cm^3), water (25 cm^3) and brine (25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give the *tosylate* (0.86 g, 77%); R_f (EtOAc–hexane, 1:1) 0.58; ν_{max}(film)/cm^{-1} 3290 (≡CH), 2115 (C≡C), 1597 (aromatic C=C) and 1176 (S=O); δ_H(250 MHz; $CDCl_3$) 7.78 (2 H, d, *J* 8.3, *o*-SArH), 7.34 (2 H, d, *J* 8.3, *m*-SArH), 4.10 (2 H, t, *J* 7.2, CH_2O), 2.44 (3 H, s, MePh), 2.03 (2 H, d, *J* 2.6, CH_2C≡C), 1.95 (1 H, dt, *J* 2.6, HC≡C), 1.70 (2 H, t, *J* 7.2, CH_2CH_2O) and 0.96 (6 H, s, Me_2C).

5,5-Dimethyloct-1-en-7-yn-3-ol. This was prepared from the aldehyde **1f** (0.63 g, 5.1 mmol), vinylmagnesium bromide (1.0 mol dm^{-3} in THF, 7 cm^3) and THF (15 cm^3) as for 3,3-dimethylhex-5-yn-1-ol, to give the *alcohol* (0.73 g, 94%); R_f (EtOAc–hexane, 1:1) 0.62; ν_{max}(film)/cm^{-1} 3380 (OH), 3310 (≡CH) and 2125 (C≡C) and 1640 (C=C); δ_H(250 MHz; $CDCl_3$) 5.89 (1 H, ddd, *J* 6.1, 10.3 and 16.8, C*H*=CH_2), 5.22 (1 H, dt, *J* 17.1 and 1.3, CH_AH_B=C), 5.06 (1 H, dt, *J* 10.3 and 1.2, CH_AH_B=C), 4.26 (1 H, br s, C*H*OH), 2.20 (2 H, m, CH_2C≡C), 2.00 (1 H, t, *J* 2.6, HC≡C), 1.55 (2 H, m, CH_2COH), 1.06 (3 H, s, $Me_A$$Me_B$C) and 1.04 (3 H, s, $Me_A$$Me_B$C).

5,5-Dimethyloct-1-en-7-yn-3-yl acetate 1h. This was prepared from 5,5-dimethyloct-1-en-7-yn-3-ol (0.70 g, 4.6 mmol), 4-dimethylaminopyridine (0.35 g, 2.9 mmol), acetic anhydride (0.63 g, 6.2 mmol, 0.60 cm^3) and dichloromethane (8 cm^3) as in the preparation of the acetate **1g**. Chromatography (SiO_2, EtOAc–hexane, 5:95) gave the *acetate* (0.61 g, 68%); R_f (EtOAc–hexane,1:9) 0.36; ν_{max}(film)/cm^{-1} 3300 (≡CH), 2120 (C≡C), 1740 (C=O) and 1650 (C=C); δ_H(250 MHz; $CDCl_3$) 5.76 (1 H, ddd, *J* 6.3, 10.4 and 17.0, C*H*=CH_2), 5.37 (1 H, tddd, *J* 1.2, 3.7, 6.3 and 8.7, C*H*CH=CH_2), 5.20 (1 H, dt, *J* 17.2 and 1.1, CH_AH_B=C), 5.11 (1 H, dt, *J* 10.4 and 1.0, CH_AH_B=C), 2.10 (2 H, d, *J* 2.8, CH_2C≡C), 2.04 (3 H, s, $MeCO_2$), 1.99 (1 H, t, *J* 2.7, HC≡C), 1.75 (1 H, dd, *J* 8.6 and 14.8, CH_AH_BCOAc), 1.60 (1 H, dd, *J* 3.7 and 14.8, CH_AH_BCOAc) and 1.00 (6 H, s, Me_2C) (Found: C, 74.45; H, 9.6. $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.35%).

Methyl (*E*)-5,5-dimethyloct-2-en-7-ynoate 1i. Following Shing,[36] methyl (triphenylphosphoranylidene)acetate (1.67 g, 5.0 mmol) was added in 10 portions over 15 min with stirring to the aldehyde **1f** (0.55 g, 4.4 mmol) in methanol (25 cm^3) under argon at 0 °C, and stirred for 1.5 h. The solvent was removed under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 2:98) to give successively the *cis-ester* (0.22 g, 27%); R_f (EtOAc–hexane, 1:9) 0.42; ν_{max}(film)/cm^{-1} 3310 (OH), 2130 (C≡C), 1730 (C=O) and 1650 (C=C); δ_H(250 MHz; $CDCl_3$) 6.26 (1 H, dt, *J* 7.8 and 11.7, CH_2C*H*=C), 5.87 (1 H, dt, *J* 1.6 and 11.7, C=C*H*CO_2Me), 3.69 (3 H, s, MeO), 2.71 (2 H, dd, *J* 1.6 and 7.8, CH_2CH=C), 2.11 (2 H, d, *J* 2.65, CH_2C≡C), 1.99 (1 H, t, *J* 2.65, HC≡C) and 1.01 (6 H, s, Me_2C) (Found: C, 73.2; H, 8.95. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.95%), and the *trans-ester* (0.38 g, 48%); R_f (EtOAc–hexane, 1:9) 0.33; ν_{max}(film)/cm^{-1} 3310 (OH), 2130 (C≡C), 1730 (C=O) and 1660 (C=C); δ_H(250 MHz; $CDCl_3$) 6.95 (1 H, dt, *J* 7.8 and 15.5, CH_2C*H*=C), 5.86 (1 H, dt, *J* 1.3 and 15.5, C=C*H*CO_2Me), 3.72 (3 H, s, MeO), 2.21 (2 H, dd, *J* 1.3 and 7.9, CH_2CH=C), 2.07 (2 H, d, *J* 2.6, CH_2C≡C), 2.00 (1 H, t, *J* 2.6, HC≡C) and 0.99 (6 H, s, Me_2C) (Found: C, 73.45; H, 8.85).

2-(1,1-Dimethylbut-3-ynyl)oxirane 1c. Following Matteson,[25] as with the oxirane **1e**, 2,2-dimethylpent-4-ynal[37] (0.74 g, 6.0 mmol) gave the *epoxide* (0.15 g, 18%); bp 50 °C/18 mmHg; R_f (EtOAc–hexane,1:9) 0.95; ν_{max}(film)/cm^{-1} 3296 (≡CH) and 2116 (C≡C); δ_H(250 MHz; $CDCl_3$) 2.84 (1 H, br t, *J* 3.4, Me_2C*H*O), 2.64 (2 H, m, CH_2O), 2.18 (1 H, dd, *J* 2.6 and 16.7, CH_AH_BC≡C), 2.12 (1 H, dd, *J* 2.7 and 16.7, CH_AH_BC≡C), 1.97 (1 H, t, *J* 2.7, HC≡C), 0.94 (3 H, s, $Me_A$$Me_B$C) and 0.93 (3 H, s, $Me_A$$Me_B$C).

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Paper 8/09813A