A Regioselective and Stereospecific Synthesis of Allylsilanes from Secondary Allylic Alcohol Derivatives

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Primary and secondary allylic acetates and benzoates react with the dimethyl(phenyl)silyl-cuprate reagent to give allylsilanes, provided that the THF in which the cuprate is prepared is diluted with ether before addition of the allylic ester. The reaction is reasonably regioselective in some cases: (i) when the allylic system is more-substituted at one end than the other, as in the reactions **4** → **5** and **9** → **10**; (ii) when the steric hindrance at one end is neopentyl-like, as in the reactions **15** → **16**; and (iii) when the disubstituted double bond has the *Z* configuration, as in the reactions *Z*-**19** → *E*-**21** or, better, because the silyl group is becoming attached to the less-sterically hindered end of the allylic system, *Z*-**20** → *E*-**22**. The regioselectivity is better if a phenyl carbamate is used in place of the ester, and a three-step protocol assembling the mixed cuprate on the leaving group is used, as in the reactions **23** → **24** and *E*- or *Z*-**29** → *E*-**21**, or, best of all, because the silyl group is again becoming attached to the less-sterically hindered end of the allylic system, *E*- or *Z*-**30** → *E*-**22**. This sequence works well to move the silyl group onto the more substituted end of an allyl system, but only when the move is from a secondary allylic carbamate to a tertiary allylsilane, as in the reaction **38** → **39**. Allyl(trimethyl)silanes can be made using alkyl- or aryl-cuprates on trimethylsilyl-containing allylic esters and carbamates, as in the reactions **40** → **41**, and **43** → **44**. The reaction of the silyl-cuprate with allylic esters and the three-step sequence with the allylic carbamates are stereochemically complementary, the former being stereospecifically *anti* and the latter stereospecifically *syn*. Homochiral allylsilanes can be made by these methods with high levels of stereospecificity, as shown by the synthesis of the allylsilanes **54**, **58** and **59**.

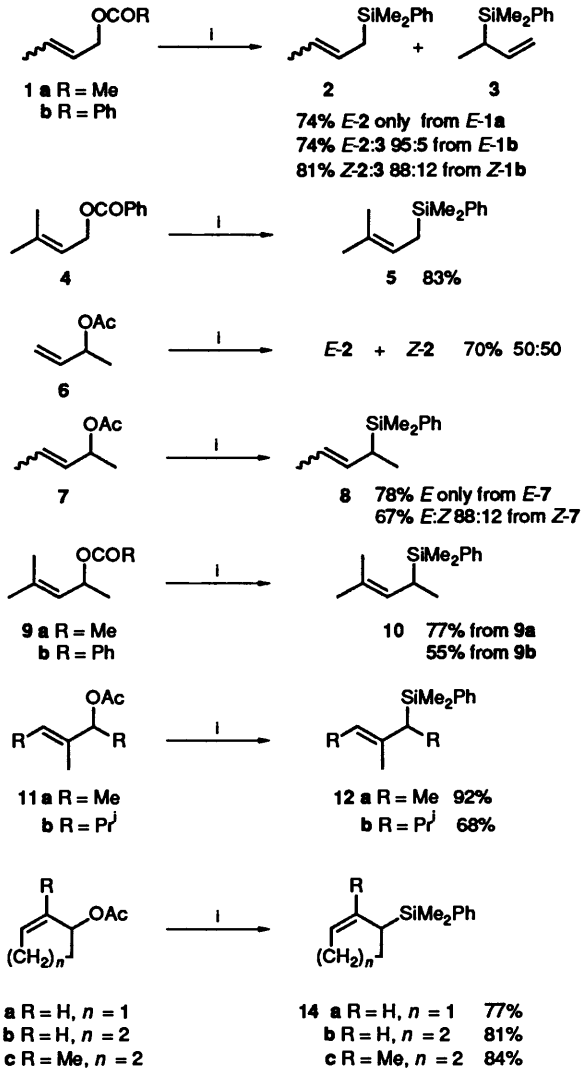
Allylsilanes undergo electrophilic substitution reactions regiospecifically in the S_E2' sense,[1] and stereospecifically in an *anti* sense, as shown, principally, by the work of Wetter,[2] Eschenmoser,[3] Kumada,[4] Kitching[5] and ourselves.[6] To take full advantage of the highly stereospecific and regiospecific reactions of allylsilanes, and anticipating a need to test whether the osmylation, epoxidation, Simmons–Smith reaction,[7] hydroboration[8] and protodesilylation[9] of allylsilanes, reported in the three preceding papers to this one, might be similarly well controlled, we sought new ways of making allylsilanes. There are, of course, many ways of making allylsilanes,[10] but it was imperative that the new routes should be both regiocontrolled and stereocontrolled, for which there were no general methods. In this paper and that following, we describe two such routes, the first using allylic alcohols as substrates, and the second using diastereoselective aldol reactions followed by stereospecific decarboxylative eliminations.[11] We have reported some of the present work using allylic alcohol derivatives in two preliminary communications.[12]

We had already established[13] a simple synthesis of allylsilanes from the reaction of tertiary allylic acetates with our silyl-cuprate reagent. This synthesis was stereospecifically *anti*,[6] and completely regioselective, giving the allylsilane with the silyl group at the less-substituted end of the allyl fragment. However, we, and Kitching,[14] had found that the silyl-cuprate reagent failed to react with secondary allylic acetates, limiting this synthesis to those allylsilanes that are disubstituted at C-3, which we already knew were apt to be unreliable in their electrophilic reactions, both stereochemically[15] and with respect to their undergoing clean S_E2' reactions.[16] Both problems stem from the ease with which an electrophile can attack at C-2 in competition with the normal preference for attack at C-3, a problem that does not arise with allylsilanes monosubstituted at C-3. Trost has found that this type of allylsilane can be prepared from secondary allylic acetates using tristrimethylsilylaluminium and transition metal catalysts,[17] and Kitching[14] and Smith[18] have found that silyl-lithium and silyl-cuprate reagents react with primary and secondary allyl chlorides. All three methods achieve some, but not complete regiocontrol.

Results and Discussion

Taking our lead from reports that a less polar solvent was better for cuprate reactions,[19] we added ether or a mixture of ether and pentane to the silyl-cuprate reagent, which we find can only be prepared in THF. In this solvent mixture, the primary and secondary allylic acetates or benzoates **1**, **4**, **6**, **7**, **9**, **11** and **13** gave the corresponding allylsilanes **2**, **3**, **5**, **8**, **10**, **12** and **14** (Scheme 1). These reactions, together with our earlier results,[14] encompass nearly the full range, with a primary, secondary or tertiary centre carrying the leaving group, a primary, secondary or tertiary centre at the other end of the double bond and a secondary or tertiary centre at the central carbon atom. The only combinations that we have not tried are those with a primary carbon at both ends and a tertiary carbon at both ends.

1. *Regioselectivity with Unsymmetrical Acetates.*—Of the reactions of the allylic esters in Scheme 1 having any regiochemistry, the allylic esters **1**, **4**, **6** and **9** regioselectively gave very largely or only the corresponding allylsilanes with the silyl group at the less-substituted end of the allylic fragment. The secondary allylic acetate **6** gave a 50:50 mixture of the *E*-and *Z*-crotylsilanes **2a**, while the stereochemistry of the double bond in the *E*-crotyl acetate *E*-**1a** was retained in the formation of the *E*-crotylsilane **2**. Only the *Z*-crotyl benzoate *Z*-**1b** gave a substantial amount (10% of the mixture) of the allylsilane **3** with the silyl group at the more-substituted end. There was no marked difference between the acetates and benzoates, when we used both, but in one case (see below), we obtained a higher yield from a benzoate.



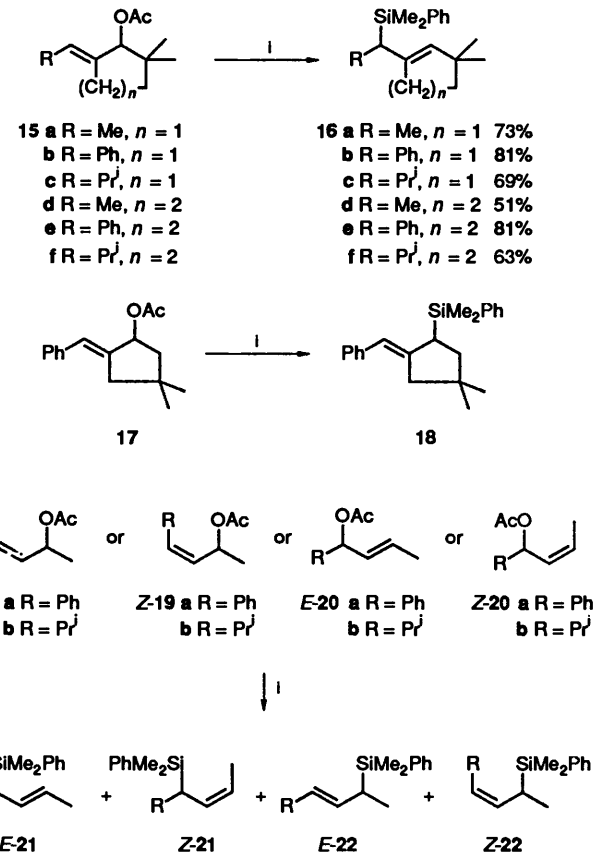
Scheme 1 *Reagent:* i, $(PhMe_2Si)_2CuCNLi_2$, THF–Et_2O (or THF–Et_2O–pentane)

Table 1 Regioselectivity in the formation of the allylsilanes **21** and **22** from the unsymmetrical allylic acetates **19** and **20**

Starting material	R	Yield (%)	Proportions of the products[a]			
			E-**21**	*Z*-**21**	*E*-**22**	*Z*-**22**
E-**19a**	Ph	40	8	23	69	
(*E*-**19a**)[b]	Ph	71	12	13	75	
E-**20a**	Ph	40	68		32	
Z-**19a**	Ph	60	88	12		
(*Z*-**19a**)[c]	Ph	90	86	14		
Z-**20a**	Ph	51		18	82	
E-**19b**	Pr^i	86	10		90	
E-**20b**	Pr^i	83	26		74	
Z-**19b**	Pr^i	55	73		8	18
(*Z*-**19b**)[c]	Pr^i	90	78		4	17
Z-**20b**	Pr^i	83			100	

[a] Estimated from distinctive signals in ^1H NMR spectra. [b] Methanesulfonate in place of acetate. [c] Benzoate in place of acetate.

The problem of regioselectivity becomes more acute when the allylic fragment is secondary at both ends (Scheme 2). There is no problem when the difference between the two ends is large, as with the neopentyl-like acetates **15**. In these cases the regioselectivity is highly in favour of the allylsilane **16** having the endocyclic double bond and the silyl group avoiding the



Scheme 2 *Reagent:* i, $(PhMe_2Si)_2CuCNLi_2$, THF–Et_2O–pentane

neopentyl position. We had thought that the clean regiochemistry in these cases might have been the result of a combination of the steric hindrance at the carbon atom in the ring and an energetically favourable change from an exocyclic double bond in the starting material **15** to an endocyclic double bond in the product **16**. However, the cyclic allylic acetate **17**, which is not significantly more hindered at one end than the other, gave largely the allylsilane **18** with an exocyclic double bond, implying that there is some preference for direct displacement of the acetoxy group, in contrast to Smith's result[18] with her trimethylsilyl-copper reagent and allylic chlorides. This is borne out by the results with the unsymmetrical *E*-allylic acetates *E*-**19** and **20**, which are also not significantly different sterically at each end. The *E*-allylic acetates gave, as the major products (Table 1), the allylsilanes from direct substitution of the acetoxy group in three of the four cases. In contrast, the *Z*-allylic acetates *Z*-**19** and **20** gave largely, in all four cases, the *E*-products of allylic displacement. In these cases, evidently, the move of the double bond from a *cis* configuration in the starting material to a *trans* configuration in the product is energetically favourable enough to influence the regiochemistry. When the move of the double bond coincides with the arrival of the silyl group at the less hindered end of the allylic fragment, as in the conversions of *Z*-**20a** and *Z*-**20b** into *E*-**22a** and *E*-**22b**, respectively, the reaction is regiochemically clean enough to be useful.

However, the most striking feature of the results in Table 1 is that the ratios of the four regioisomeric products are considerably different with each starting material, in contrast to the corresponding reactions of lithium dimethylcuprate with the acetates *E*-**19a** and *E*-**20a**, both of which are known to give largely (*E*)-3-methyl-1-phenylbut-1-ene, with only the smallest differences from one starting material to the other.[20] Goering did not report the reaction of lithium dimethylcuprate with the

Table 2 Regioselectivity in the formation of the allylsilanes **21** and **22** from the unsymmetrical allylic urethanes **29** and **30**

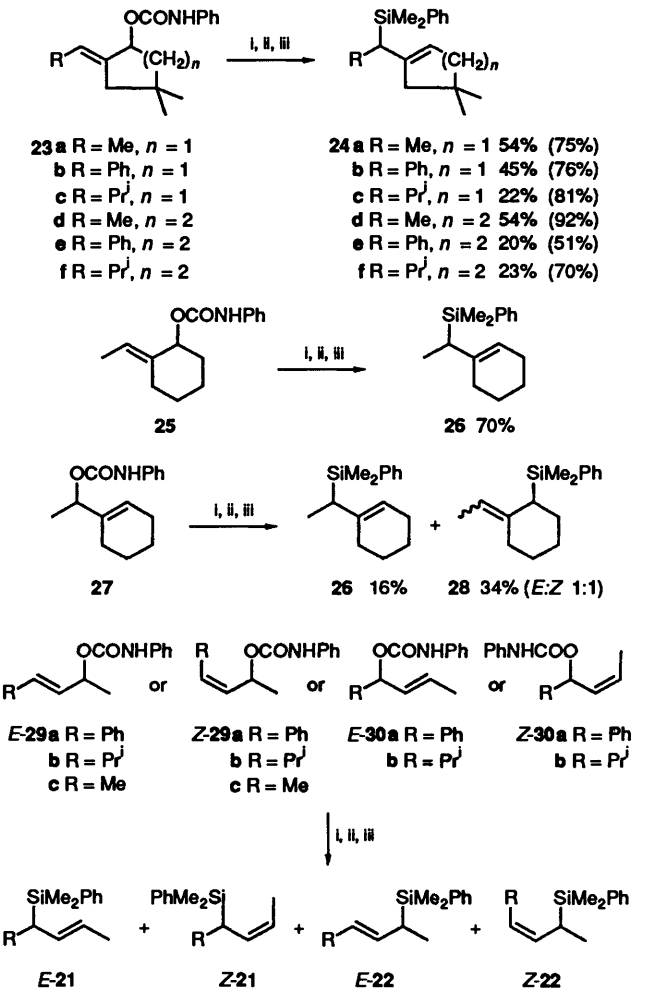
Starting material	R	Yield (%)	Proportions of the products[a]			
			E-**21**	*Z*-**21**	*E*-**22**	*Z*-**22**
E-**29a**	Ph	68	39	8	52	
Z-**29a**	Ph	75	100			
Z-**30a**	Ph	68			100	
E-**29b**	Pr^i	86	67	9	23	
E-**30b**	Pr^i	87			100	
Z-**29b**	Pr^i	64	100			
Z-**30b**	Pr^i	87			100	
E-**29c**	Me	75	82	18	—	—
Z-**29c**	Me	82	98	2	—	—

[a] Estimated from distinctive signals in ^{1}H NMR spectra.

Z-acetates *Z*-**19a** and *Z*-**20a**, but we find that they also give largely (*E*)-3-methyl-1-phenylbut-1-ene. Such tiny differences in product distribution as are discernible in Goering's work with alkyl cuprates match ours with the silyl cuprate: there is a trend towards direct displacement in the *E*-isomers[20,21] and towards allylic shift in the *Z*-isomers.[22] Clearly, the intermediate allyl cuprates, thought to be involved in this type of reaction, are not completely equilibrated in our reaction, as they evidently are, almost completely, with alkyl cuprates. This reflects the greater rate of the reductive elimination step when one of the ligands on the copper(III) intermediate is a silyl group and a silicon–carbon bond is being forced. That a relatively electropositive element should undergo faster reductive elimination is consistent with our observations[23] that mixed alkyl-silyl cuprates selectively transfer the silyl group rather than the alkyl group in all their reactions, and that a mixed stannyl-alkyl cuprate and a mixed silyl-stannyl cuprate selectively transfer the stannyl group, in all of which reactions a reductive elimination step can be presumed to occur. It is also clear that the intermediates in our work are σ-allyl species, retaining the distinction between the two ends of the allylic fragment found in the starting materials, and not π-allyl species, where this distinction is necessarily lost. This matches the observation with alkyl cuprates that a better leaving group than acetate leads to a greater degree of direct displacement.[21] In line with this, we find that the mesylate corresponding to the acetate *E*-**19a** gave a slightly higher proportion of the allylsilane *E*-**22a** than the acetate did. Although the improvement in the yield was considerable, the improvement in regioselectivity was marginal. In any case, this cannot be a general solution to the regiocontrol problem, because all attempts to make the mesylate corresponding to *E*-**20a** gave the mesylate corresponding to *E*-**19a**.

The reactions in the **a** series (R^1 = Ph) gave the allylsilanes **21a** and **22a** (Scheme 2) in rather low yields. Later, when studying the corresponding reactions in the **b** series (R^1 = Pr^i), we discovered that the addition of triphenylphosphine, which is known to stabilise cuprates,[24] improved the yields. These reactions are somewhat capricious, as cuprate reactions frequently are, and adding phosphine or pentane did not always make much difference. Most of the reactions in Scheme 1, for example, took place in good yield without any need for added phosphine. It is probably good advice to suggest that one should try the reaction first without either pentane or phosphine, and bear in mind that either or both may help if the yield proves to be low. The ether, however, is essential. Insofar as we have duplicated runs with and without triphenylphosphine and with tributylphosphine in place of triphenylphosphine, we find little difference in the regioselectivities in Table 1. We also found little difference in regioselectivity or yield with various added Lewis acids. The reaction with *Z*-**19b** was notably low-yielding (55%) with attack at the acetyl group accounting for most of the loss. It was in this case that we discovered that the corresponding benzoate gave a better yield (90%) with little effect on the distribution of regioisomers.

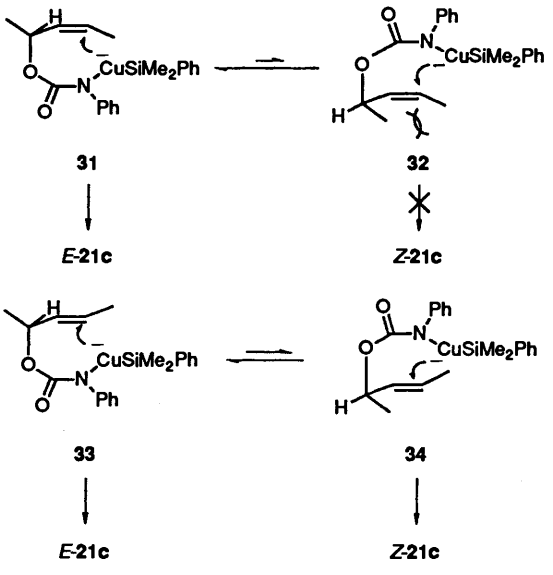
2. *Regioselectivity using a Three-step Sequence on Carbamates.*—Although useful levels of regiocontrol can be achieved using the *Z*-allylic acetates, we were not satisfied, and turned to the possibility that the corresponding carbamates might be better. Carbamates allow a cuprate reagent to be assembled on the leaving group, in consequence of which the cuprate is delivered intramolecularly largely to the allylic position. We applied the sequence introduced by Galina and Ciattini[25] for alkyl cuprates, and refined by Goering,[26] to our silyl cuprates. The results for the allylic systems that are secondary at both ends (Scheme 3 and Table 2), show that the regiocontrol



Scheme 3 *Reagents:* i, BuLi, THF; ii, CuI; iii, $PhMe_2Li$

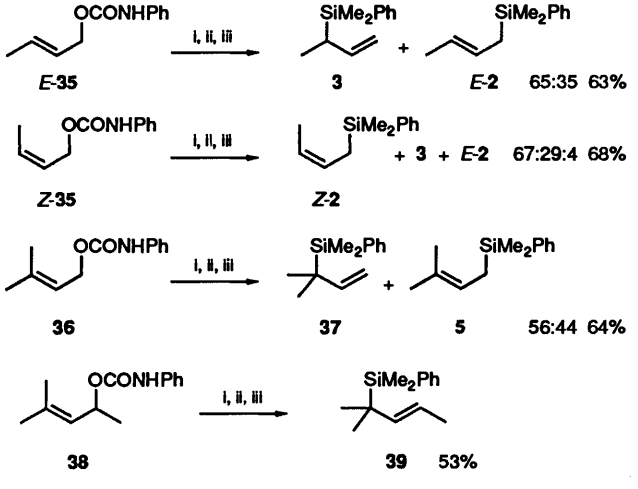
problem is largely solved, although the yields are sometimes low, with much starting material recovered in such cases. The yields shown in parentheses in Scheme 3 are those based on starting material consumed. The allylic carbamates **23** and **25** with exocyclic double bonds consistently gave the allylsilanes **24** and **26** with endocyclic double bonds; but the carbamate **27** with an endocyclic double bond gave a mixture of the regioisomeric allylsilanes **26** and **28**, with the latter an equal mixture of *E*- and *Z*-isomers, and the carbamate *E*-**29a** gave virtually no regioselectivity. We did not succeed in preparing the carbamate *E*-**30a**, because the corresponding alcohol reacted with phenyl isocyanate to give the rearranged carbamate *E*-**29a**. Otherwise the reactions are fairly well-

behaved regiochemically. The two substrates that have no regiochemistry **29c** show that the *Z*-allylic system more strongly favours the formation of the *E*-product. This is easily understandable: the two reasonable conformations **31** and **32** for reaction from the *Z*-isomer are very different in energy, because of the $A^{1,3}$ strain in **32**, but the two conformations **33** and **34** of the *E*-isomer are closer in energy. This analysis



supports the generally accepted picture of internal delivery of the cuprate, with predominant allylic inversion.

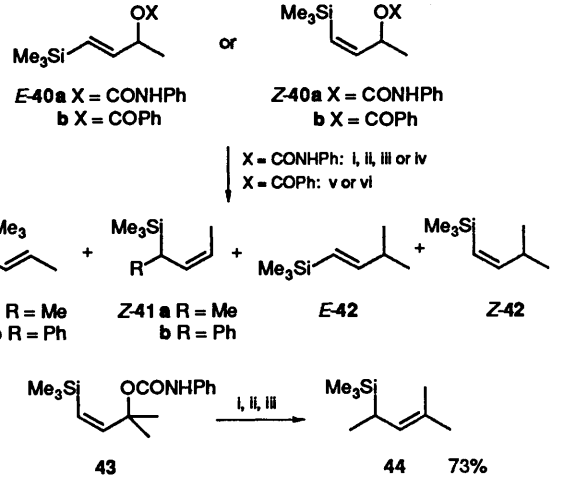
The same sequence of steps also works to some extent with allylic systems having unsymmetrical levels of substitution on the allylic fragment (Scheme 4), overpowering the tendency for



Scheme 4 *Reagents:* i, BuLi, THF; ii, CuI; iii, $PhMe_2SiLi$

these systems simply to give the product with the silyl group at the less-substituted end of the allylic fragment, as in our earlier work [13] and in those examples in Scheme 1 that have any regiochemistry. The major products from the carbamates *E*-**35**, **36** and **38** are the allylsilanes **3**, **37** and **39**, respectively, with the silyl group at the more-substituted end, but the selectivity is only synthetically useful in the last of these. Surprisingly, the *Z*-crotyl carbamate *Z*-**35** is less selective than the *E*-isomer *E*-**35** in placing the silyl group at the more-substituted end of the allylic fragment, with the major product in this case *Z*-**2** being that of direct displacement. Because we have already developed a method for the synthesis of the allylsilanes **3** and **37**,[27] our failure to make them cleanly in this work is less important than it might be. That method, however, was only developed for the synthesis of allylsilanes having a terminal methylene group, and is not available for the synthesis of allylsilanes like **39**, for which the present method is uniquely effective.

In all the work described above, we used the dimethyl(phenyl)silyl group as the nucleophile, in the form of its readily available cuprate. Some of this chemistry will, no doubt, work for its trimethylsilyl counterpart, but the trimethylsilyllithium reagent can only be prepared easily in HMPA, and its derived cuprate therefore is dissolved in a relatively polar solvent. Since the key feature of our success with the allylic acetates is in having a less polar solvent, it will not be surprising that some at least of the work described here will not work for the synthesis of allyl(trimethyl)silanes. One solution to this problem, which has some precedent,[28] and which we have already applied to the synthesis of allenyl(trimethyl)silanes,[29] is to incorporate the trimethylsilyl group into the allylic substrate, and use an alkyl or aryl cuprate as the nucleophile. We have tested the feasibility of this approach to a limited extent (Scheme 5 and Table 3). The



Scheme 5 *Reagents:* i, BuLi or MeLi, THF; ii, CuI; iii, MeLi; iv, PhLi; v, MeCuCN Li, Et_2O; vi, Me_2CuLi

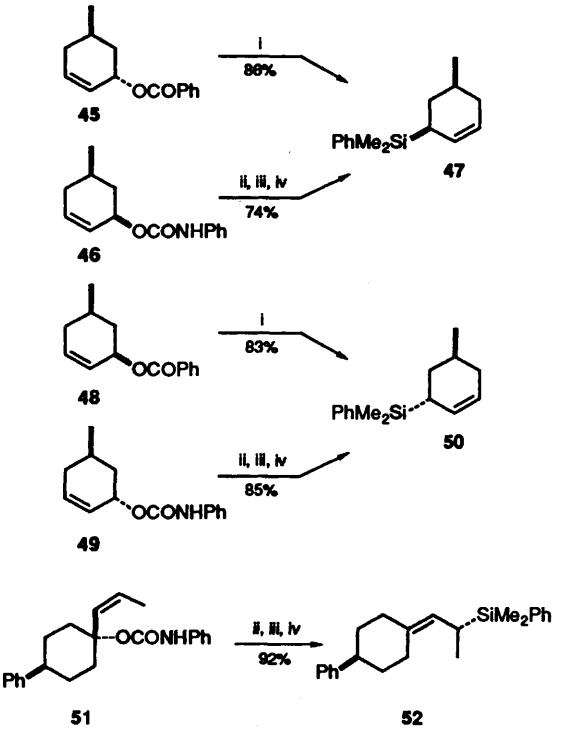
carbamate technique works well with the *Z*-carbamates *Z*-**40a** and **43**, giving cleanly the allylsilanes *E*-**41** and **44**, respectively. with the *E*-carbamate *E*-**40a** only a little worse than *Z*-**40a**, in giving some of the *Z*-allylsilane *Z*-**41a**. The *Z*-benzoate *Z*-**40b** was little worse than *Z*-**40a**, in giving some of the *Z*-allylsilane *Z*-**41a**. The *Z*-benzoate *Z*-**40b** was also clean in giving allylic displacement, but only with the heterocuprate derived from one equivalent of methyllithium and one of copper(I) cyanide, a cuprate known to be more selective for allylic displacement.[30] The *E*-benzoate *E*-**40b** gave a mixture of products with this cuprate, but was comparatively clean in giving the vinylsilane *E*-**42** with the standard lithium dimethylcuprate.

3. *Stereochemistry.*—We had every expectation that the reactions described above would be well-controlled stereochemically. We already knew that tertiary allylic acetates reacted with our silyl-cuprate reagent stereospecifically *anti*,[6] and it was also known that the carbamate sequence was stereospecifically *syn* with alkyl and aryl cuprates.[26] We confirmed that there were no surprises in store by carrying out the reactions in Scheme 6. The secondary allylic benzoates **45** and **48** cleanly gave the known [14] allylsilanes **47** and **50**, respectively, by *anti* displacement, and the diastereoisomeric carbamates **46** and **49** gave the same allylsilanes **47** and **50**, respectively, by *syn* displacement. These racemic compounds, of course, do not reveal the regiochemistry of the reaction, which is probably only

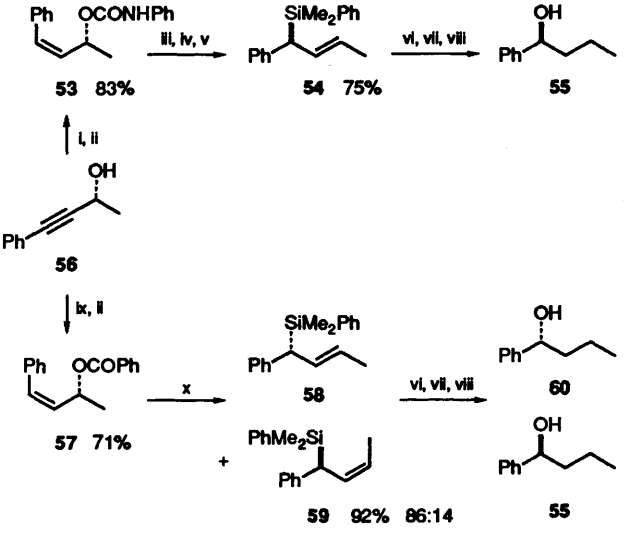
Table 3 Regioselectivity in the formation of the allylsilanes **41** and **42** from the unsymmetrical allylic urethanes and benzoates **40**

Starting material	X	Cuprate	R	Yield (%)	Proportions of the products[a]			
					E-**41**	*Z*-**41**	*E*-**42**	*Z*-**42**
E-**40a**	CONHPh	*b*	Me	40	90	10		
Z-**40a**	CONHPh	*b*	Me	74	100			
E-**40a**	CONHPh	*c*	Ph	59	93	7		
Z-**40a**	CONHPh	*c*	Ph	87	100			
E-**40b**	COPh	Me_2Cu Li	Me	44	6		91	3
Z-**40b**	COPh	Me_2Cu Li	Me	69	59		4	38
E-**40b**	COPh	MeCuCN Li	Me	52	55	30	15	
Z-**40b**	COPh	MeCuCN Li	Me	55	98		1	1

[a] Estimated from distinctive signals in ^{1}H NMR spectra. [b] Three-step sequence using MeLi, see Scheme 5. [c] Three-step sequence using PhLi, see Scheme 5.



Scheme 6 *Reagents:* i, $(PhMe_2Si)_2CuCN\ Li_2$; ii, BuLi, THF; iii, CuI; iv, $PhMe_2SiLi$



Scheme 7 *Reagents:* i, PhNCO, Et_3N; ii, H_2, $Pd/BaSO_4$, quinoline; iii, BuLi, THF; iv, CuI; v, $PhMe_2SiLi$; vi, H_2, Pd/C; vii, BF_3·2AcOH; viii, MCPBA, Et_3N; ix, $(PhCO)_2O$, Et_3N, DMAP; x, $(PhMe_2Si)_2CuCN\ Li_2$

clean for the carbamates, but they do reveal the complementary nature of the two processes that make it possible to synthesise either allylsilane from the same allylic alcohol. The tertiary allylic carbamate **51** also gave the known[6] allylsilane **52** from *syn* displacement.

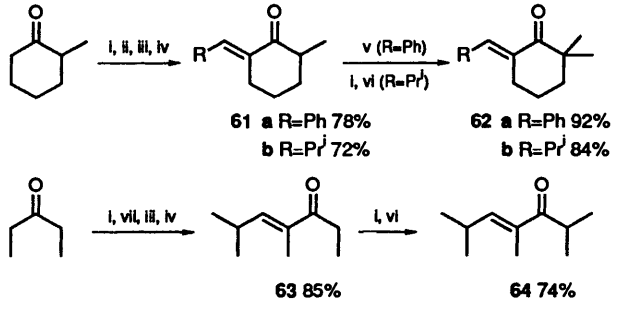
With the methods in hand, we now ventured to make our first homochiral allylsilanes, deliberately choosing another example that would reveal the complementarity of the two allylsilane syntheses. The propargyl alcohol **56**, readily available in 78% e.e. by reduction of the corresponding ketone with Alpine-borane,®[31,32] gave the carbamate **53**, which cleanly gave the allylsilane **54**. We proved the sense of chirality and degree of optical purity in this compound by reducing the double bond, and converting the dimethyl(phenyl)silyl group into a hydroxy group with retention of configuration.[33] The known[34] (−)-alcohol **55** was produced in 72% e.e., as measured by ^{1}H NMR spectroscopy of its Mosher's ester,[35] only a little less than that of the starting material. The same propargyl alcohol **56** gave the benzoate **57**, which gave a mixture of the *E*- and *Z*-allylsilanes **58** and **59**, in a ratio similar to that from the racemic acetates (Table 1). We did not separate this mixture, but converted it directly into the mixture of enantiomeric alcohols **60** and **55**, which were present in a ratio of 76:24 (52% e.e.). Allowing for the silicon-substituted centres in the *E*- and *Z*-allylsilanes **58** and **59** having opposite absolute configurations, this level of optical purity is again very close (96%) to that expected for a completely stereospecific reaction. Thus, all the conversions in Scheme 7 are almost certainly, within experimental error, highly stereospecific.

At first sight, the formation of the mixture of allylsilanes **58** and **59** does not look helpful, but these allylsilanes, differing from each other in *two* stereochemical features, the stereogenic centre and the double bond geometry, will react with electrophiles to give the *same* enantiometer of the product of an S_E2' reaction. Thus, either enantiomer of an S_E2' product can, in principle, be made from a single propargyl alcohol. Alternatively, convergence is possible—one enantiomer (or diastereoisomer) of a propargyl alcohol can be converted into either enantiomer (or diastereoisomer) of the corresponding allylsilane, and the other enantiomer (or diastereoisomer) of the propargyl alcohol can then be converted into the *same* allylsilane. When we used convergence to control the configuration of an allylsilane in our Prelog–Djerassi lactone synthesis,[36] we achieved convergence using a different method—control of the double bond geometry of the allylic acetate. This had the disadvantage that we needed to use a reduction of the triple bond with lithium aluminium hydride in order to make the *E*-allylic acetate. The new method, using the different *Z*-allylic alcohol derivatives, avoids the need for this effectively undiscriminating reagent.

4. *Preparation of the Starting Materials.*—Almost all of the starting materials used in this work were prepared uneventfully by standard methods. The acetates and benzoates were prepared from the corresponding alcohols using acetic anhydride

or chloride or benzoic anhydride, triethylamine and *N,N*-dimethylaminopyridine (DMAP)[37] in the usual way. Likewise, the carbamates were prepared from the alcohols using phenyl isocyanate and triethylamine. The open-chain *E*-allylic alcohols were prepared by the reaction of a lithium or Grignard reagent on the α,β-unsaturated aldehyde. The open-chain *Z*-allylic acetates, benzoates or carbamates were prepared by hydrogenation of the corresponding propargylic derivatives, themselves prepared from the alcohols obtained by treating the saturated aldehydes with lithium acetylides.[38] The alcohol precursors to the cyclic allylic acetates and carbamates, and to the open-chain acetates **11a** and **11b**, were prepared by Luche reduction[39] of the α,β-unsaturated ketones, which were, in turn, prepared, when the double bond was exocyclic, by base-catalysed condensation of the cyclic ketone with the appropriate aldehyde.

Only the following points are worthy of note. In the preparation of the precursors to the carbamates **23a–c**, 3,3-dimethylcyclopentanone was rather unselective regiochemically in its reaction with base, in contrast to Posner's experience with a closely similar compound,[40] and the mixtures of enones eventually derived from the mixture of enolates had to be separated by extensive chromatography. We prepared 2,2-dimethylcyclohexanone, the precursor to the acetate **15d**, by phenylthiomethylation–desulfurisation.[41] Because this route gave us some trouble in the Raney nickel step, we used a slightly different order of events, illustrated in Scheme 8, in order to



Scheme 8 *Reagents:* i, LDA; ii, RCHO; iii, $MeSO_2Cl$, Et_3N; iv, DBU; v, $KOBu^t$, MeI; vi, MeI; vii, Pr^iCHO

prepare the precursors **62a** and **62b** of the acetates **15e** and **15f**. A similar sequence also served for the preparation of the precursor **64** of the acetate **11b**. The same problem did not arise with 2,2-dimethylcyclopentanone, which we prepared by hydrogenation of 5,5-dimethylcyclopent-2-enone.[42] The β-hydroxy ketones, in general, were better dehydrated by treatment with methanesulfonyl chloride followed by base, which gave only the *E*-isomers, than by treatment with acid[43] which gave *E*- and *Z*-mixtures and some equilibration of the double bond into the ring.[44] The alcohol precursor to the *cis*-benzoate **48** was even more the major product (98:2) from reduction of the corresponding ketone when the reaction with lithium aluminium hydride was carried out at −78 °C instead of at 0 °C.[45] The *trans*-benzoate **45** was the major, but not quite the exclusive product, from Mitsunobu reaction[46] with the diastereoisomeric *cis*-alcohol and benzoic acid.

Experimental

General Method for the Synthesis of Allylsilanes from Allylic Acetates and Benzoates.—Typically, dimethyl(phenyl)-silyllithium[47] (1.0 mol dm^{-3} solution in THF; 6.0 cm^3) was added to a stirred slurry of copper(I) cyanide (3.0 mmol) and triphenylphosphine (6.0 mmol) in ether (15 cm^3) or a mixture of ether and pentane (15 cm^3, 1:1) under nitrogen at 0 °C. After 20 min, the allylic acetate or benzoate (2.0–3.0 mmol) in ether (5 cm^3) or a mixture of ether and pentane (5 cm^3, 1:1) was added dropwise over 5 min. The mixture was stirred at 0 °C for a further 2–4 h, quenched with aqueous ammonium chloride and extracted with ether. The ether layer was washed with aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was chromatographed (hexane) to remove the fast-running silicon-containing by-products and/or distilled to give the allylsilane. The following allylsilanes were made by this method.

(E)-1-*Dimethyl(phenyl)silylbut-2-ene*[48] E-**2** (74% *from* E-**1a**) (74% *as a* 95:5 *mixture with* **3** *from* E-**1b**) (70% *as a* 50:50 *mixture with* Z-**2** *from* **6**). R_f (hexane) 0.46; ν_{max}(film)/cm^{-1} 1247 (SiMe), 1113 (SiPh) and 964 (*trans*-CH=CH); δ_H($CDCl_3$) 7.54–7.33 (5 H, m, Ph), 5.40–5.25 (2 H, m, CH=CH), 1.66–1.61 (5 H, m, CH_2 and Me) and 0.26 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 139.1, 133.6, 128.7, 127.7, 126.4, 124.0, 21.7, 17.9 and −3.3; *m/z* 190 (2%, M^+), 135 (100, $PhMe_2Si$) and 55 (20, M − $PhMe_2Si$) (Found: M^+, 190.1175. $C_{12}H_{18}Si$ requires *M*, 190.1178).

(Z)-1-*Dimethyl(phenyl)silylbut-2-ene* Z-**2** (81% *of a* 74:10:16 *mixture with* E-**2** *and* E-**3** *from an* 86:14 *mixture of* Z-**1b** *and* E-**1b**). R_f (hexane) 0.46; ν_{max}(film)/cm^{-1} 1241 (SiMe), 1111 (SiPh) and 1011 (C=C); δ_H($CDCl_3$) 7.7–7.2 (5 H, m, Ph), 5.7–5.2 (2 H, m, CH=CH), 1.77 (2 H, d, *J* 7, CH_2Si), 1.56 (3 H, d, *J* 5, MeC=C) and 0.34 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 134.0, 133.8, 128.9, 127.8, 125.8, 122.1, 17.1, 12.5 and −3.3; *m/z* 190 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 190.1174. $C_{12}H_{18}Si$ requires *M*, 190.1178).

1-*Dimethyl(phenyl)silyl-3-methylbut-2-ene*[49] **5** (83% *from* **4**). R_f(hexane) 0.43; ν_{max}(film)/cm^{-1} 1258 (SiMe) and 1128 (Si-Ph); δ($CDCl_3$) 7.7–7.2 (5 H, m, Ph), 5.17 (1 H, t quintet, *J* 8.2 and 1.2, Me_2C=C*H*), 1.69 (3 H, d, *J* 1.2, Me_AMe_BC=C), 1.65 (2 H, d, *J* 8.2, CH_2Si), 1.51 (3 H, d, *J* 1.2, Me_A*Me*$_B$C=C) and 0.27 (6 H, s, $SiMe_2$); *m/z* 204 (14%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 204.1331. $C_{13}H_{20}Si$ requires *M*, 204.1334) identical (^1H NMR) with an authentic sample prepared from 2-methylbut-3-en-2-yl acetate by the method of Marchi.[13]

(E)-2-*Dimethyl(phenyl)silyl-3-ene* E-**8** (78% *from* E-**7**) (67% *of an* 88:12 *mixture with* Z-**8** *from* Z-**7**). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1251 (SiMe), 1116 (SiPh) and 975 (*trans*-CH=CH); δ_H($CDCl_3$) 7.52–7.32 (5 H, m, Ph), 5.43 (1 H, ddq, *J* 15.3, 7.0 and 1.4, MeCH=C*H*), 5.23 (1 H, ddq, *J* 15.3, 1.2 and 6.2, 1.2, MeC*H*=CH), 1.75 (1 H, quintet of quintets, *J* 7.5 and 1.2, SiCH), 1.65 (3 H, dt, *J* 6.2 and 1.4, *Me*CH=CH), 1.02 (3 H, d, *J* 7.4, SiCH*Me*) and 0.24 (6 H, s, $SiMe_2$); δ_C($CDCl_3$) 138.2, 134.0, 133.6, 128.8, 127.6, 121.4, 25.7, 17.9, 14.1, −4.7 and −5.3; *m/z* 204 (3%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 204.1320. $C_{13}H_{20}Si$ requires *M*, 204.1334).

2-*Dimethyl(phenyl)silyl-4-methylpent-3-ene*[50] **10** (77% *from* **9a**) (55% *from* **9b**). R_f (hexane) 0.44; ν_{max}(film)/cm^{-1} 1260 (SiMe), 1117 (SiPh) and 999 (C=C); δ($CDCl_3$) 7.6–7.2 (5 H, m, Ph), 4.95 (1 H, d septet, *J* 10.8 and 1.4, Me_2C=C*H*), 1.95 (1 H, dq, *J* 10.8 and 7.1, MeC*H*Si), 1.68 (3 H, d, *J* 1.4, CMe_AMe_B), 1.44 (3 H, d, *J* 1.4, CMe_A*Me*$_B$), 0.97 (3 H, d, *J* 7.1, SiCH*Me*), 0.26 (3 H, s, SiMe_AMe_B) and 0.24 (3 H, s, $SiMe_A$*Me*$_B$); δ_C($CDCl_3$) 138.3, 134.0, 128.2, 127.5, 127.4, 25.9, 21.9, 18.1, 15.4, −4.6 and −5.5; *m/z* 218 (3%, M^+), 135 (100, $PhMe_2Si$) and 105 (7, PhSi) (Found: M^+, 218.1499. $C_{14}H_{22}Si$ requires *M*, 218.1491).

(E)-4-*Dimethyl(phenyl)silyl-3-methylpent-2-ene* **12a** (92%). R_f (hexane) 0.47; ν_{max}(film)/cm^{-1} 1252 (SiMe) and 1115 (SiPh); δ_H($CDCl_3$) 7.51–7.31 (5 H, m, Ph), 5.01 (1 H, br q, *J* 6.5, C=CH), 1.75 (1 H, q, *J* 7.5, SiCH), 1.56 (3 H, d, *J* 6.5, =CH*Me*), 1.46 (3 H, t, *J* 1.0, CMe) 1.06 (3 H, d, *J* 7.5, SiCH*Me*), 0.30 (3 H, s, SiMe_AMe_B) and 0.28 (3 H, s, $SiMe_A$*Me*$_B$); δ_C($CDCl_3$) 138.9, 138.4, 133.9, 128.7, 127.5, 116.0, 31.8, 17.0, 14.4, 13.4, −3.9 and −4.7; *m/z* 218 (5%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 218.1483. $C_{14}H_{22}Si$ requires *M*, 218.1491).

(E)-5-*Dimethyl(phenyl)silyl-2,4,6-trimethylhept-3-ene* **12b** (68%). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1630 (C=C); δ-($CDCl_3$) 7.53–7.28 (5 H, m, Ph), 4.82 (1 H, dq, *J* 9 and 1, HC=C),

2.44 (1 H, d septet, *J* 9 and 7, $Me_2CHC{=}C$), 1.88 (1 H, d septet, *J* 8 and 7, $Me_2CHCHSi$), 1.46 (3 H, d, *J* 1, $MeC{=}C$), 1.34 (1 H, d, *J* 8, CHSi), 0.91 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.84 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.82 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.81 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.35 (3 H, s, $SiMe_AMe_B$) and 0.22 (3 H, s, $SiMe_AMe_B$); *m/z* 274 (22%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 274.2130. $C_{18}H_{30}Si$ requires *M*, 274.2117).

3-*Dimethyl(phenyl)silylcyclopentene* **14a** (77%). R_f(hexane) 0.37; ν_{max}(film)/cm^{-1} 1240 (SiMe) and 1105 (SiPh); δ_H($CDCl_3$) 7.54–7.32 (5 H, m, Ph), 5.66 (2 H, m, CH=CH), 2.30–1.80 (5 H, m, ring H), 0.26 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 138.7, 133.7, 132.0, 128.9, 128.5, 127.7, 34.1, 33.0, 25.3, −4.57 and −4.60; *m/z* 202 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 202.1175. $C_{13}H_{18}Si$ requires *M*, 202.1178).

3-*Dimethyl(phenyl)silylcyclohexene* **14b** (81%). R_f(hexane) 0.40; ν_{max}(film)/cm^{-1} 1640 (C=C), 1245 (SiMe) and 1105 (SiPh); δ_H($CDCl_3$) 7.55–7.33 (5 H, m, Ph), 5.65 (2 H, m, CH=CH), 1.97–1.45 (7 H, m, ring H), 0.30 (3 H, s, $SiMe_AMe_B$) and 0.28 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 138.3, 134.0, 128.9, 127.7, 126.0, 127.6, 25.7, 25.1, 23.9, 22.6, −4.6 and −4.7; *m/z* 216 (5%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 216.1340. $C_{14}H_{20}Si$ requires *M*, 216.1334).

3-*Dimethyl(phenyl)silyl-2-methylcyclohexene* **14c** (84%). R_f(hexane) 0.40; ν_{max}(film)/cm^{-1} 1659 (C=C), 1248 (SiMe) and 1111 (SiPh); δ_H($CDCl_3$) 7.56–7.32 (5 H, m, Ph), 5.32 (1 H, m, C=CH), 2.0–1.4 (7 H, m, ring H), 1.55 (3 H, d, *J* 1.8, C=CMe), 0.35 (3 H, s, $SiMe_AMe_B$) and 0.31 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 139.8, 135.3, 133.7, 128.6, 127.6, 120.2, 30.1, 25.5, 25.1, 21.4, −2.4 and −2.5; *m/z* 230 (8%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 230.1493. $C_{15}H_{22}Si$ requires, *M*, 230.1491).

1-[1-*Dimethyl(phenyl)silylethyl*]-3,3-*dimethylcyclopentene* **16a** (73%). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1630 (C=C); δ-($CDCl_3$) 7.50–7.29 (5 H, m, Ph), 4.91 (1 H, s, HC=C), 2.13–1.81 (5 H, m, CH_2CH_2, CHSi), 1.06 (3 H, d, *J* 7, *Me*CHSi), 0.97 (6 H, s, Me_2) and 0.27 (6 H, s, Me_2Si); *m/z* 205 (11%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 258.1797. $C_{17}H_{26}Si$ requires *M*, 258.1804).

1-[α-*Dimethyl(phenyl)silylbenzyl*]-3,3-*dimethylcyclopentene* **16b** (81%). R_f(hexane) 0.21; ν_{max}(film)/cm^{-1} 1640 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.5–7.2 (10 H, m, Ph), 5.2 (1 H, m, HC=C), 3.1 (1 H, s, CHSi), 2.2 (2 H, t, *J* 7, $CH_2CH_2C{=}C$), 1.5 (2 H, t, *J* 7, $CH_2CH_2C{=}C$), 0.9 (6 H, s, Me_2) and 0.3 (6 H, s, $SiMe_2$); *m/z* 320 (4%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 320.1951. $C_{22}H_{28}Si$ requires *M*, 320.1960).

1-[1-*Dimethyl(phenyl)silyl-2-methylpropyl*]-3,3-*dimethylcyclopentene* **16c** (69%). R_f(hexane) 0.46; ν_{max}(film)/cm^{-1} no C=C detected; δ($CDCl_3$) 7.54–7.27 (5 H, s, Ph), 4.97 (1 H, s, HC=C), 2.07 (2 H, t, *J* 6, $CH_2CH_2C{=}C$), 1.89 (1 H, m, Me_2CH), 1.56–1.45 (3 H, m, $CH_2CH_2C{=}C$ and CHSi), 1.00 (3 H, s, CMe_AMe_B), 0.91 (3 H, s, CMe_AMe_B), 0.84 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.83 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.34 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); *m/z* 286 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 286.2102. $C_{19}H_{30}Si$ requires *M*, 286.2117).

1-[1-*Dimethyl(phenyl)silylethyl*]-3,3-*dimethylcyclohexene* **16d** (51%). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1650 (C=C); δ($CDCl_3$) 7.56–7.27 (5 H, m, Ph), 4.89 (1 H, s, HC=C), 2.04–1.94 (2 H, m, $CH_2C{=}C$), 1.65–1.19 (5 H, m, CH_2CH_2, CHSi), 0.92 (3 H, s, CMe_AMe_B), 0.89 (3 H, s, CMe_AMe_B), 0.81 (3 H, d, *J* 7, *Me*CHSi), 0.27 (3 H, s, $SiMe_AMe_B$) and 0.24 (3 H, s, $SiMe_AMe_B$); *m/z* 272 (4%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 272.1971. $C_{18}H_{28}Si$ requires *M*, 272.1960).

1-[α-*Dimethyl(phenyl)silylbenzyl*]-3,3-*dimethylcyclohexene* **16e** (81%). R_f(hexane) 0.25; ν_{max}(film)/cm^{-1} 1600 and 1500 (Ph); δ($CDCl_3$) 7.41–7.02 (10 H, m, Ph), 5.27 (1 H, s, HC=C), 2.88 (1 H, s, CHSi), 1.80–1.69 (2 H, m, $CH_2C{=}C$), 1.52–1.30 (4 H, m, CH_2CH_2), 0.94 (3 H, s, CMe_AMe_B), 0.92 (3 H, s, CMe_AMe_B), 0.31 (3 H, s, $SiMe_AMe_B$) and 0.27 (3 H, s, $SiMe_AMe_B$); *m/z* 334 (5%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 394.2086. $C_{28}H_{30}Si$ requires *M*, 394.2117).

1-[1-*Dimethyl(phenyl)silyl-2-methylpropyl*]-3,3-*dimethylcyclohexene* **16f** (43%, *with* 32% *recovered acetate*). R_f(hexane) 0.44; ν_{max}(film)/cm^{-1} no C=C detected; δ($CDCl_3$) 7.56–7.28 (5 H, m, Ph), 4.95 (1 H, s, HC=C), 1.98–1.77 (1 H, m, Me_2CH), 1.66–1.62 (2 H, m, $CH_2C{=}C$), 1.56–1.20 (5 H, CH_2CH_2, CHSi), 0.92 (3 H, s, CMe_AMe_B), 0.85 (3 H, s, CMe_AMe_B), 0.82 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.81 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.24 (3 H, s, $SiMe_AMe_B$); *m/z* 300 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 300.2293. $C_{20}H_{32}Si$ requires *M*, 300.2273).

cis-3-*Dimethyl(phenyl)silyl-5-methylcyclohexene*[14] **47** (86% *from* **45**). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1257 (SiMe) and 1126 (SiPh); δ_H($CDCl_3$) 7.6–7.3 (5 H, m, Ph), 5.7–5.6 (2 H, m, CH=CH), 2.1–1.5 (5 H, m, remainder), 1.07 (1 H, dt, *J* 12.6 and 11.4, CH_AH_BCSi *cis* to Me), 0.94 (3 H, d, *J* 6.0, Me), 0.31 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 134.0, 128.9, 127.7, 127.2, 127.1, 126.1, 34.0, 32.7, 29.5, 26.5, 22.4, −4.9 and −5.3; *m/z* 230 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 230.1497. $C_{15}H_{22}Si$ requires *M*, 230.1490). This allylsilane (74%, as a 95:5 mixture with its *trans* isomer) was also prepared from carbamate **46** by the standard preparation.

trans-3-*Dimethyl(phenyl)silyl-5-methylcyclohexene*[14] **50** (83% *from* **48**). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1260 (SiMe) and 1126 (SiPh); δ_H($CDCl_3$) 7.6–7.3 (5 H, m, Ph), 5.7–5.5 (2 H, m, CH=CH), 2.2–1.3 (6 H, m, remaining ring H's), 0.88 (3 H, d, *J* 6.3, MeC), 0.30 (3 H, s, $SiMe_AMe_B$) and 0.29 (3 H, s, $SiMe_AMe_B$); δ_C($CDCl_3$) 133.9, 128.9, 127.7, 127.3, 124.3, 33.0, 31.2, 26.2, 24.9, 21.1 and −4.1; *m/z* 230 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 230.1479. $C_{15}H_{22}Si$ requires *M*, 230.1490). This allylsilane (85%) was also prepared from the carbamate **49** by the standard preparation.

General Method for the Synthesis of Allylsilanes from Allylic Carbamates.—Butyllithium (1.5 mol dm^{-3} solution in hexane; 2.2 cm^3) was added to the carbamate (3 mmol) in THF (5 cm^3) under argon at 0 °C, or better, in some cases, at −78 °C, and the mixture stirred for 1 min. It was then transferred to a flask containing copper(I) iodide (3.1 mmol) and triphenylphosphine (6.2 mmol) in ether (5 cm^3) under argon at 0 °C and stirred for 30 min. Dimethyl(phenyl)silyllithium (1.0 mol dm^{-3} solution in THF; 4.6 cm^3) was added to the mixture which was then stirred for a further 2 h. After aqueous ammonium chloride (30 cm^3) had been added to the mixture it was extracted with ether (2 × 30 cm^3). The combined ether extracts were washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (hexane) to remove the fast-running silicon-containing by-products and to give the allylsilane. The following allylsilanes were made by this method.

1-[1-*Dimethyl(phenyl)silylethyl*]-4,4-*dimethylcyclopentene* **24a** (54%, *with* 28% *recovered carbamate*). R_f(hexane) 0.44; ν_{max}(film)/cm^{-1} 1640 (C=C); δ($CDCl_3$) 7.50–7.25 (5 H, m, Ph), 5.00 (1 H, m, HC=C), 2.07 (2 H, d, *J* 2, $CH_2C{=}C$), 1.92 (1 H dd, *J* 12 and 2, $CH_AH_BC{=}C$), 1.90 (1 H, dd, *J* 12 and 2, $CH_AH_BC{=}C$), 1.82 (1 H, q, *J* 7, CHSi), 1.06 (3 H, d, *J* 7, MeCH), 1.00 (3 H, s, CMe_AMe_B), 0.99 (3 H, s, CMe_AMe_B), 0.28 (3 H, s, $SiMe_AMe_B$) and 0.27 (3 H, s, $SiMe_AMe_B$); *m/z* 258 (7%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 258.1808. $C_{17}H_{26}Si$ requires *M*, 258.1804).

1-[α-*Dimethyl(phenyl)silylbenzyl*]-4,4-*dimethylcyclopentene* **24b** (45%, *with* 41% *recovered carbamate*). R_f(hexane) 0.18; ν_{max}(film)/cm^{-1} 1630 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.49–7.02 (10 H, m, Ph), 5.30 (1 H, s, HC=C), 3.10 (1 H, s, CHSi), 2.11 (2 H, m, $CH_2C{=}C$), 2.01 (1 H, d, *J* 15, $CH_AH_BC{=}C$), 1.97 (1 H, d, *J* 15, $CH_AH_BC{=}C$), 0.99 (3 H, s,

CMe_AMe_B), 0.98 (3 H, s, CMe_AMe_B), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); *m/z* 320 (10%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 320.1958. $C_{22}H_{28}Si$ requires *M*, 320.1960).

1-[1-*Dimethyl(phenyl)silyl*-2-*methylpropyl*]-4,4-*dimethylcyclopentene* **24c** (22%, *with* 73% *recovered carbamate*). R_f(hexane) 0.46; ν_{max}(film)/cm^{-1} 1650 (C=C); $\delta(CDCl_3)$ 7.57–7.25 (5 H, m, Ph), 5.26 (1 H, t, *J* 2, HC=C), 2.06 (2 H, m, CH_2C=C), 1.9 (2 H, m, CH_2C=C), 1.85 (1 H, m, CHSi), 1.65 (1 H, m, Me_2CH), 1.01 (3 H, s, CMe_AMe_B), 0.97 (3 H, s, CMe_AMe_B), 0.86 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.84 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.36 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); *m/z* 286 (13%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 286.2142. $C_{19}H_{30}Si$ requires *M*, 286.2117).

1-[1-*Dimethyl(phenyl)silylethyl*]-5,5-*dimethylcyclohexene* **24d** (54%, *with* 41% *recovered carbamate*). R_f(hexane) 0.31; ν_{max}(film)/cm^{-1} 1660 (C=C); $\delta(CDCl_3)$ 7.50–7.29 (5 H, m, Ph), 5.14 (1 H, m, HC=C), 1.99 (2 H, m, CH_2C=C), 1.62 (1 H, q, *J* 7, MeCHSi), 1.55 (2 H, CH_2CH_2C=C), 1.22 (2 H, t, *J* 6, CH_2CH_2C=C), 1.04 (3 H, d, *J* 7, *Me*CHSi), 0.82 (3 H, s, CMe_AMe_B), 0.79 (3 H, s, CMe_AMe_B), 0.27 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); *m/z* 272 (8%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 272.1955. $C_{18}H_{28}Si$ requires *M*, 272.1960).

1-[α-*Dimethyl(phenyl)silylbenzyl*]-5,5-*dimethylcyclohexene* **24e** (20%, *with* 61% *recovered carbamate*). R_f(hexane) 0.23; ν_{max}(film)/cm^{-1} 1640 (C=C), 1600, 1580 and 1500 (Ph); $\delta(CDCl_3)$ 7.41–7.27 (10 H, m, Ph), 5.53 (1 H, m, HC=C), 2.86 (1 H, m, CHSi), 2.03 (2 H, m, CH_2C=C), 1.64 (2 H, m, CH_2CH_2C=C), 1.21 (2 H, t, *J* 6, CH_2CH_2C=C), 0.80 (3 H, s, CMe_AMe_B), 0.76 (3 H, s, CMe_AMe_B), 0.31 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); *m/z* 334 (7%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 334.2137. $C_{23}H_{30}Si$ requires *M*, 334.2117).

1-[1-*Dimethyl(phenyl)silyl*-2-*methylpropyl*]-5,5-*dimethylcyclohexene* **24f** (23%, *with* 67% *recovered carbamate*). R_f(hexane) 0.37; ν_{max}(film)/cm^{-1} 1640 (C=C); $\delta(CDCl_3)$ 7.53–7.27 (5 H, m, Ph), 5.25 (1 H, m, HC=C), 2.03–1.83 (3 H, m, CH_2C=C and Me_2CH), 1.59–1.50 (2 H, m, CH_2C=C), 1.45–1.20 (3 H, m, CH_2CH_2C=C and CHSi), 0.90 (12 H, m, 4 × Me), 0.35 (3 H, s, $SiMe_AMe_B$) and 0.32 (3 H, s, $SiMe_AMe_B$); *m/z* 300 (3%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 300.2290. $C_{20}H_{32}Si$ requires *M*, 300.2273).

1-[1-*Dimethyl(phenyl)silylethyl*]*cyclohexene* **26** (44%, *with* 37% *recovered carbamate*). R_f(hexane) 0.46; ν_{max}(film)/cm^{-1} 1650 (C=C), 1250 (SiMe) and 1113 (SiPh); $\delta_H(CDCl_3)$ 7.51–7.30 (5 H, m, Ph), 5.19 (1 H, m, HC=C), 1.98 (2 H, m, ring H), 1.71 (2 H, m, ring H), 1.59 (1 H, q, *J* 7.5, SiCH), 1.50 (4 H, m, ring H), 1.06 (3 H, d, *J* 7.5, SiCH*Me*), 0.28 (3 H, s, $SiMe_AMe_B$) and 0.25 (3 H, s, $SiMe_AMe_B$); $\delta_C(CDCl_3)$ 140.4, 138.8, 133.9, 128.7, 127.5, 118.7, 30.1, 29.8, 25.4, 23.2, 22.7, 14.3, −4.0 and −4.6; *m/z* 244 (6%, M^+) and 135 (100, $PhMe_2Si$) and 108 (20, M − $PhMe_2SiH$) (Found: M^+, 244.1631. $C_{16}H_{24}Si$ requires *M*, 244.1647).

(E-) *and* (Z)-1-*Dimethyl(phenyl)silyl*-2-*ethylidenecyclohexane* E-**28**, Z-**28** *and* **26** (0.51 g, 51%) *in a* 1:1:1 *ratio as an inseparable mixture*. R_f(hexane) 0.46; ν_{max}(film)/cm^{-1} 1250 (SiMe) and 1110 (SiPh); $\delta_H(CDCl_3)$ 7.54–7.30 (15 H, m, Ph), 5.19 (1 H, m, C=CH), 5.11 (1 H, br q, *J* 5.5 with fine coupling, C=C*H*Me), 5.00 (1 H, q, *J* 6.7, C=C*H*Me), 2.50–1.10 (12 H, m, ring Hs and C=CH*Me*), 1.39 (3 H, dd, *J* 7.5, SiCH*Me*), 0.39 (3 H, s, $SiMe_AMe_B$), 0.34 (3 H, s, $SiMe_AMe_B$), 0.30 (3 H, s, $SiMe_AMe_B$), 0.28 (6 H, s, $SiMe_2$) and 0.25 (3 H, s, $SiMe_AMe_B$) (in addition to the signals from **26**); *m/z* 244 (3.4%, M^+), 135 (100, $PhMe_2Si$) and 108 (20, M − $PhMe_2SiH$) (Found: M^+, 244.1659. $C_{16}H_{24}Si$ requires *M*, 244.1647).

(E)-1-*Dimethyl(phenyl)silyl*-1-*phenylbut*-2-*ene* E-**21a** (75% *from* Z-**29a**). R_f(hexane) 0.35; ν_{max}(film)/cm^{-1} 1257 (SiMe), 1126 (SiPh) and 975 (C=C); $\delta(CDCl_3)$ 7.5–6.8 (10 H, m, 2 × Ph), 5.77 (1 H, ddq, *J* 15.1, 9.3 and 1.3, C*H*=CHMe), 5.33 (1 H, ddq, *J* 0.6, 15.1 and 5.9, CH=C*H*Me), 3.08 (1 H, d quintet, *J* 9.3 and 0.6, C*H*Si), 1.68 (3 H, ddd, *J* 5.9, 1.3 and 0.6, MeC=C), 0.27 (3 H, s, $SiMe_AMe_B$) and 0.24 (3 H, s, $SiMe_AMe_B$); $\delta_C(CDCl_3)$ 142.4, 137.2, 134.3, 130.0, 128.9, 128.0, 127.4, 124.5, 42.5, 18.0, −4.2 and −4.7; *m/z* 266 (6%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 266.1504. $C_{18}H_{22}Si$ requires *M*, 266.1491).

(E)-3-*Dimethyl(phenyl)silyl*-2-*methylhex*-4-*ene* E-**21b** (64% *from* Z-**29b**. R_f(hexane) 0.35; ν_{max}(film)/cm^{-1} 1247 (SiMe), 1111 (SiPh) and 971 (C=C); $\delta(CDCl_3)$ 7.6–7.3 (5 H, m, Ph), 5.35 (1 H, dd, *J* 15.5 and 9.8, C*H*=CHMe), 5.23 (1 H, dq, *J* 15.5 and 5.4, CH=C*H*Me), 1.80 (1 H, d septet, *J* 4.9 and 6.7, C*H*Me_2), 1.68 (3 H, d, *J* 5.4, MeC=C), 1.60 (1 H, dd, *J* 9.8 and 4.9, Pr^iCHSi), 0.83 (6 H, d, *J* 6.7, Me_2CH), 0.30 (3 H, s, $SiMe_AMe_B$) and 0.27 (3 H, s, $SiMe_AMe_B$); *m/z* 232 (1%, M^+), 135 (100, $PhMe_2Si$) and 96 (16, M − $PhMe_2SiH$) (Found: M^+, 232.1658. $C_{15}H_{24}Si$ requires *M*, 232.1647).

(E)-2-*Dimethyl(phenyl)silyl*-4-*phenylbut*-3-*ene* E-**22a** (68% *from* Z-**30a**). R_f(hexane) 0.35; ν_{max}(film)/cm^{-1} 1249 ($SiMe_2$), 1117 (SiPh) and 977 (C=C); $\delta(CDCl_3)$ 7.7–7.1 (10 H, m, 2 × Ph), 6.31 (1 H, dd, *J* 16 and 5, C*H*=CHPh), 6.16 (1 H, dd, *J* 16 and 2, CH=C*H* Ph), 2.06 (1 H, ddq, *J* 2, 5 and 7, MeC*H*Si), 1.19 (3 H, d, *J* 7, *Me*CHSi), 0.35 (3 H, s, $SiMe_AMe_B$) and 0.34 (3 H, s, $SiMe_AMe_B$); *m/z* 266 (6%, M^+), 135 (100, $PhMe_2Si$) and 91 (10, C_7H_7) (Found: M^+, 266.1485. $C_{18}H_{22}Si$ requires *M*, 266. 1491).

(E)-2-*Dimethyl(phenyl)silyl*-5-*methylhex*-3-*ene* E-**22b** (87% *from* E- *or* Z-**30b**). R_f(hexane) 0.45; ν_{max}(film)/cm^{-1} 1248 (SiMe), 1112 (SiPh) and 974 C=C); $\delta(CDCl_3)$ 7.6–7.3 (5 H, m, Ph), 5.38 (1 H, ddd, *J* 15.4, 7.7 and 0.9, CH=C*H*CHSi), 5.18 (1 H, ddd, *J* 15.4, 6.7 and 0.9, C*H*=CHCHSi), 2.26 (1 H, d octet, *J* 0.9 and 6.7, C*H*Me_2), 1.75 (1 H, ddq, *J* 0.9, 7.7 and 7.3, C*H*Si), 1.04 (3 H, d, *J* 7.3, *Me*CHSi), 0.97 (6 H, d, *J* 6.7, Me_2CH) and 0.27 (6 H, s, $SiMe_2$); *m/z* 232 (2%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 232.1633. $C_{15}H_{24}Si$ requires *M*, 232.1647).

(E)-2-*Dimethyl(phenyl)silyl*-2-*methylpent*-3-*ene* **39** (53%). R_f (hexane) 0.45; ν_{max}(film)/cm^{-1} 1259 (SiMe), 1127 (SiPh) and 990 (C=C); $\delta(CDCl_3)$ 7.6–7.2 (5 H, m, Ph), 5.46 (1 H, dq, *J* 15.4 and 1.0, C*H*=CHMe), 5.08 (1 H, dq, *J* 15.4 and 5.8, CH=C*H*Me), 1.68 (3 H, dd, *J* 5.8 and 1, MeC=C), 0.97 (6 H, s, Me_2CSi) and 0.26 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 139.1, 137.5, 134.7, 128.8, 127.3, 120.0, 25.5, 23.1, 18.2 and −6.0; *m/z* 218 (3%, M^+), 135 (100, $PhMe_2Si$), 84 (15, M − $PhMe_2Si$ + H), 68 (16, M − $PhMe_2Si$ − Me) and 55 (18, M − $PhMe_2Si$ − C_2H_4) (Found: M^+, 218.1486. $C_{14}H_{22}Si$ requires *M*, 218.1491).

(RS,SR)-[2-*Dimethyl(phenyl)silylpropylidene*]-4-*phenylcyclohexane* **52** (92%). M.p. 38–40 °C; identical (m.p., ^{13}C NMR) with an authentic sample.[6]

The following silanes, identified only by the part or all of their ^1H NMR spectra given below, were produced as minor components of product mixtures.

3-*Dimethyl(phenyl)silylbut*-1-*ene*[27] **3**. $\delta_H(CDCl_3)$ 7.7–7.2 (5 H, m, Ph), 5.95 (1 H, ddd, *J* 17, 12 and 8, C*H*=CH_2), 4.95 (1 H, dt, *J* 12 and 2, C=CH_AH_B), 4.90 (1 H, dt, *J* 17 and 2, C=CH_AH_B), 1.95 (1 H, m, CHSi), 1.15 (3 H, d, *J* 8, MeCSi) and 0.40 (6 H, s, $SiMe_2$); $\delta_C(CDCl_3)$ 27.2, 13.1, −5.0 and 5.4; $\delta_C(CDCl_3)$ 141.2, 137.9, 134.0, 129.0, 127.7, 110.6, 27.2, 13.2, −4.9 and −5.4.

(Z)-2-*Dimethyl(phenyl)silylpent*-3-*ene* Z-**8**. $\delta(CDCl_3)$ 7.6–7.3 (5 H, m, Ph), 5.5–5.1 (2 H, m, CH=CH), 2.10 (1 H, dq, *J* 10.5 and 7.2, CHSi), 1.46 (3 H, dd, *J* 6.5 and 1.5, MeC=C), 1.00 (3 H, d, *J* 7.2, *Me*CHSi), 0.27 (3 H, s, $SiMe_AMe_B$) and 0.26 (3 H, s, $SiMe_AMe_B$) matching the ^1H NMR spectrum of the authentic sample reported in the following paper.

(Z)-1-*Dimethyl(phenyl)silyl*-1-*phenylbut*-2-*ene* Z-**21a**. $\delta(CDCl_3)$ 7.5–6.9 (10 H, m, 2 × Ph), 5.79 (1 H, ddq, *J* 11.4, 10.8 and 1.7, C*H*=CHMe), 5.48 (1 H, dq, *J* 10.8 and 6.7, CH=C*H*Me),

3.45 (1 H, d, *J* 11.4, PhC*H*Si), 1.47 (3 H, dd, *J* 6.7 and 1.7, MeC=C), 0.27 (3 H, s, Si*Me*$_A$Me$_B$) and 0.24 (3 H, s, SiMe$_A$*Me*$_B$) matching the ^{1}H NMR spectrum of the authentic sample reported in the following paper.

(Z)-3-*Dimethyl(phenyl)silyl*-2-*methylhex*-4-*ene* Z-**21b**. δ(CDCl$_3$) 7.6–7.2 (5 H, m, Ph), 5.65 (1 H, dq, *J* 11.0 and 6.4, CH=C*H*Me), 2.04 (1 H, dd, *J* 11.4 and 4.5, CHSi), 1.46 (3 H, dd, *J* 6.7 and 1.5, MeC=C), 0.84 (6 H, d, *J* 5.9, *Me*$_2$CH), 0.32 (3 H, s, Si*Me*$_A$Me$_B$) and 0.28 (3 H, s, SiMe$_A$*Me*$_B$) matching the ^{1}H NMR spectrum of the authentic sample reported in the following paper.

(Z)-2-*Dimethyl(phenyl)silyl*-5-*methylhex*-3-*ene* Z-**22b**. δ(CDCl$_3$) 7.6–7.2 (5 H, m, Ph), 5.2–4.9 (2 H, m, CH=CH), 2.47 (1 H, octet, *J* 7, C*H*Me$_2$), 2.10 (1 H, dq, *J* 10 and 7, CHSi), 1.02 (3 H, d, *J* 7, *Me*CHSi), 0.92 (3 H, d, *J* 7, CH*Me*$_A$Me$_B$) 0.80 (3 H, d, *J* 7, CHMe$_A$*Me*$_B$), 0.29 (3 H, s, Si*Me*$_A$Me$_B$) and 0.28 (3 H, s, SiMe$_A$*Me*$_B$) matching the ^{1}H NMR spectrum of the authentic sample reported in the following paper.

3-*Dimethyl(phenyl)silyl*-3-*methylbut*-1-*ene*[27] **37**. δ(CDCl$_3$) 7.7–7.2 (5 H, m, Ph), 5.85 (1 H, dd, *J* 17 and 11, C*H*=CH$_2$), 4.90 (1 H, dd, *J* 11 and 2, C=C*H*$_A$H$_B$), 4.75 (1 H, dd, *J* 17 and 2, C=CH$_A$*H*$_B$), 1.05 (6 H, s, Me$_2$CSi) and 0.30 (6 H, s, SiMe$_2$).

(Z)-4-*Trimethylsilylpent*-2-*ene*[51] Z-**41a**. δ(CDCl$_3$) 5.5–5.1 (2 H, m, CH=CH), 1.87 (1 H, dq, *J* 10.5 and 7.1, MeC*H*Si), 1.56 (3 H, dd, *J* 6.5 and 1.4, MeC=C), 1.02 (3 H, d, *J* 7.1, *Me*CHSi) and −0.04 (9 H, s, SiMe$_3$).

(Z)-1-*Phenyl*-1-*trimethylsilylbut*-2-*ene*[4] Z-**41b**. δ(CDCl$_3$) 7.3–7.0 (5 H, m, Ph), 5.86 (1 H, tq, *J* 11.5 and 1.8, C*H*=CHMe), 5.50 (1 H, dq, *J* 11.5 and 6.9, CH=C*H*Me), 3.28 (1 H, d, *J* 11.5, PhC*H*Si), 1.63 (3 H, dd, *J* 6.9 and 1.8, MeC=C) and 0.05 (9 H, s, SiMe$_3$).

(Z)-3-*Methyl*-1-*trimethylsilylbut*-1-*ene*[52] Z-**42**. δ(CDCl$_3$) 6.08 (1 H, dd, *J* 14 and 9, C*H*=CHSi), 5.34 (1 H, d, *J* 14, CH=C*H*Si), 2.48 (1 H, dq, *J* 9 and 6, C*H*Me$_2$), 0.95 (6 H, d, *J* 6, *Me*$_2$CH) and 0.10 (9 H, s, SiMe$_3$).

Methyl Cyano-cuprate Reaction: (E)-2-*Trimethylsilylpent*-3-*ene* E-**41a**.—Methyllithium (1.5 mol dm^{-3} in Et$_2$O; 2.4 cm^3) was added to a stirred suspension of copper(I) cyanide (325 mg, 3.6 mmol) in dry ether (8 cm^3) under nitrogen at 0 °C and the mixture stirred at 0 °C for 15 min. The benzoate *Z*-**40b** (300 mg, 1.2 mmol) in dry ether (3 cm^3) was added to the mixture which was then stirred at 0 °C for 3 h. The usual aqueous work-up procedure and chromatography (pentane) of the residue gave the allylsilane[53] (94 mg, 55%); R_f (hexane) 0.6; δ(CDCl$_3$) 5.43 (1 H, ddq, *J* 15.2, 7.7 and 1.3, C*H*=CHMe), 5.20 (1 H, ddq, *J* 15.2, 1.3 and 6.2, CH=C*H*Me), 1.65 (3 H, dt, *J* 6.2 and 1.3, MeC=C), 1.49 (1 H, dq, *J* 7.7 and 7.3, MeC*H*Si), 1.01 (3 H, d, *J* 7.3, *Me*CHSi) and −0.06 (9 H, s, SiMe$_3$). This allylsilane (0.20 g, 74%) was also prepared from the carbamate *Z*-**40a** by the standard method described for the preparation of **44**.

(E)-1-*Phenyl*-1-*trimethylsilylbut*-2-*ene* E-**41b**.—Butyllithium (1.5 mol dm^{-3} solution in hexane; 1.26 cm^3) was stirred with the carbamate *Z*-**40a** (0.5 g) in THF (15 cm^3) under nitrogen at 0 °C and copper(I) iodide (0.361 g) in THF (10 cm^3) was added to it. After 10 min, phenyllithium (1 mol dm^{-3} solution in Et$_2$O; 1.9 cm^3) was added to the mixture, which was then stirred for 3 h. The usual aqueous work-up procedure and chromatography (pentane) of the residue gave the allylsilane[4] (87%); R_f(hexane) 0.27; δ(CDCl$_3$) 7.3–7.0 (5 H, m, Ph), 5.81 (1 H, ddq, *J* 14.9, 9.9 and 1.4, C*H*=CHMe), 5.42 (1 H, dq, *J* 14.9 and 6.4, CH=C*H*Me), 2.89 (1 H, d, *J* 9.9, PhC*H*), 1.72 (3 H, dd, *J* 6.4 and 1.4, MeC=C) and −0.03 (9 H, s, SiMe$_3$).

Dimethyl Cuprate Reaction: (E)-3-*Methyl*-1-*trimethylsilylbut*-1-*ene* E-**42**.—Methyllithium (1.5 mol dm^{-3} in Et$_2$O; 2.4 cm^3) was added to a stirred suspension of copper(I) iodide (345 mg, 1.8 mmol) in dry ether (10 cm^3) under nitrogen at 0 °C. The mixture was stirred for 30 min after which the benzoate *E*-**40b** (300 mg, 1.2 mmol) in ether (5 cm^3) was added to it and stirring continued for a further 3 h at 0 °C. The usual aqueous work-up procedure and chromatography (pentane) of the residue gave the vinylsilane[52] (75 mg, 44%) as 91% of the mixture of isomers; R_f(hexane) 0.6; ν_{max}(film)/cm^{-1} 1262 (SiMe); δ(CDCl$_3$) 5.98 (1 H, dd, *J* 18.7 and 5.8, C*H*=CHSi), 5.54 (1 H, dd, *J* 18.7 and 1.3, CH=C*H*Si), 2.27 (1 H, d octet, *J* 1.3 and 5.8, C*H*Me$_2$), 0.97 (6 H, d, *J* 5.8, *Me*$_2$CH) and 0.03 (9 H, s, SiMe$_3$); *m*/*z* 142 (6%, M$^+$), 127 (35, M − Me), 99 (17, M − C$_3$H$_7$) and 73 (100, SiMe$_3$) (Found: M$^+$, 142.1178. C$_8$H$_{18}$Si requires *M*, 142.1178).

4-*Methyl*-2-*trimethylsilylpent*-3-*ene* **44**.—Methyllithium (1.5 mol dm^{-3} in Et$_2$O; 0.67 cm^3) was added to a stirred solution of the carbamate **43** (277 mg, 1.0 mmol) in dry THF (10 cm^3) under nitrogen at 0 °C. After 0.5 min, the solution was transferred to a stirred suspension of copper(I) iodide (190 mg, 1.0 mmol) in dry THF (5 cm^3) also under nitrogen at 0 °C and the mixture was stirred for 10 min. Methyllithium (1.5 mol dm^{-3} in ether; 0.67 cm^3) was added to the mixture which was then stirred for 3 h. The usual aqueous work-up procedure and chromatography of the residue (pentane) gave the *allylsilane* (114 mg, 73%); R_f (hexane) 0.6; ν_{max}(film)/cm^{-1} 1259 (SiMe) and 998 (C=C); δ(CDCl$_3$) 4.93 (1 H, d septet, *J* 10.8 and 1.4, C=CH), 1.70 (1 H, dq, *J* 10.8 and 7.0, C*H*Me), 1.69 (3 H, d, *J* 1.4, *Me*$_A$Me$_B$C=C), 1.55 (3 H, d, *J* 1.4, Me$_A$*Me*$_B$C=C), 0.98 (3 H, d, *J* 7.0, MeCH) and −0.06 (9 H, s, SiMe$_3$); *m*/*z* 156 (6%, M$^+$), 82 (6, M − SiMe$_3$H) and 73 (100, SiMe$_3$) (Found: M$^+$, 156.1322. C$_9$H$_{20}$Si requires *M*, 156.1335).

2,2-*Dimethylcyclopentanone*.—5,5-Dimethylcyclopent-2-enone[42] was stirred with 10% palladium on charcoal in methanol (100 cm^3) under hydrogen at room temp. for 6 h. The solvent was evaporated under reduced pressure to give the ketone (96%), which was identical with an authentic sample.[41]

3,3-*Dimethylcyclopentanone*.—Methyllithium (1.6 mol dm^{-3} solution in Et$_2$O; 68.3 cm^3) was added to a stirred slurry of copper(I) iodide (55.0 mmol) in ether (40 cm^3) under argon at 0 °C. 3-Methylcyclopent-2-enone (4.8 g) was added dropwise to the mixture, which was stirred for 2 h and then poured into aqueous ammonium chloride and extracted with ether. The extract was washed with brine, dried (MgSO$_4$) and evaporated under reduced pressure to give the ketone (83%), b.p. 150–152 °C (lit.,[54] 153–154 °C), identical (IR and ^{1}H NMR) with those reported.[54]

2,2-*Dimethylcyclohexanone*.—This was made by the method of Paterson[41] from 2-methyl-1-trimethylsilyloxycyclohexene.[55] The phenythiomethylation worked well (83%) but the Raney nickel desulfurisation gave the ketone (27%), identical (IR and ^{1}H NMR) with an authentic sample, in low yield on this occasion.

4,4-*Dimethylcyclohexanone*.—4,4-Dimethylcyclohex-2-enone[56] (35 mmol) and 10% palladium on charcoal were stirred in methanol (100 cm^3) under hydrogen at room temp. for 6 h. The solvent was evaporated under reduced pressure to give the ketone (94%) as needles, m.p. 38–40 °C (lit.,[57] m.p. 40–42 °C); ν_{max}(mull)/cm^{-1} 1715 (C=C); δ(CDCl$_3$) 2.3 (4 H, t, *J* 7, 2 × CH$_2$C*H*$_2$C=O), 1.6 (4 H, t, *J* 7, 2 × C*H*$_2$CH$_2$C=O) and 1.0 (6 H, s, Me$_2$).

General Method for the Synthesis of Exocyclic Enones.—A solution of the ketone (13.4 mmol) in THF (5 cm^3) was added dropwise to a stirred solution of LDA (14.7 mmol) in THF (20 cm^3) at −78 °C. After 20 min the aldehyde (MeCHO, PhCHO or Pr^{i}CHO) (16.0 mmol) was added to the solution, which was

then stirred for a further 2 h at −78 °C. After this it was quenched with aqueous ammonium chloride and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil. To this dissolved in dichloromethane were added triethylamine (30 mmol) and methanesulfonyl chloride (15 mmol) and the solution stirred at 0 °C for 1 h. DBU (30 mmol) was then added to the solution, which was then warmed to room temp. After 2 h, the reaction was quenched with aqueous ammonium chloride and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give an oil which was chromatographed (CH_2Cl_2) to give the ketone. The following α,β-unsaturated ketones were made by this method.

(E)-2-*Ethylidene*-5,5-*dimethylcyclopentanone* (74%). R_f (CH_2Cl_2) 0.38; ν_{max}(film)/cm^{-1} 1710 (C=O) and 1640 (C=C); δ($CDCl_3$) 6.62 (1 H, qt, *J* 7 and 2, HC=C), 2.48 (2 H, m, CH_2C=C), 1.82 (3 H, dt, *J* 7 and 2, MeC=C), 1.74 (2 H, t, *J* 7, CH_2), 1.03 (6 H, s, Me_2); *m*/*z* 138 (65%, M^+) and 69 (100) (Found: M^+, 138.1051. $C_9H_{14}O$ requires *M*, 138.1045).

(E)-2-*Ethylidene*-4,4-*dimethylcyclopentanone* (41%). R_f (CH_2Cl_2) 0.36; ν_{max}(film)/cm^{-1} 1710 (C=O) and 1640 (C=C); δ($CDCl_3$) 6.55 (1 H, m, HC=C), 2.32 (2 H, m, CH_2C=C), 2.12 (2 H, 2 H, s, CH_2C=O), 1.73 (3 H, dt, *J* 7, and 2, MeC=C), 1.04 (6 H, s, Me_2); *m*/*z* 138 (72%, M^+) and 123 (100, M − Me) (Found: M^+, 138.1055. $C_9H_{14}O$ requires *M*, 138.1045).

(E)-2-(2-*Methylpropylidene*)-5,5-*dimethylcyclopentanone* (82%). R_f(CH_2Cl_2) 0.40; ν_{max}(film)/cm^{-1} 1710 (C=O) and 1640; δ($CDCl_3$) 6.41 (1 H, dt, *J* 7 and 3, HC=C), 2.50 (2 H, dt, *J* 3 and 7, CH_2C=C), 2.60–2.40 (1 H, m, CHC=C), 1.72 (2 H, t, *J* 7, CH_2), 1.05 (6 H, s, Me_2CC=O), 1.02 (6 H, d, *J* 7, Me_2CH); *m*/*z* 166 (45%, M^+) and 151 (100, M − Me) (Found: M^+, 166.1358. $C_{11}H_{18}O$ requires *M*, 166.1358).

(E)-2-(2-*Methylpropylidene*)-4,4-*dimethylcyclopentanone* (43%). R_f (CH_2Cl_2) 0.42; ν_{max}(film)/cm^{-1} 1710 (C=O) and 1640 (C=C); δ($CDCl_3$) 6.35 (1 H, dt, *J* 8 and 2.5, HC=C), 2.37 (2 H, d, *J* 2.5, CH_2C=C), 2.50–2.32 (1 H, m, CHC=C), 2.14 (2 H, s, CH_2C=O), 1.07 (6 H, s, CMe_2), 1.00 (6 H, d, *J* 7, Me_2CH); *m*/*z* 166 (35%, M^+) and 151 (100, M − Me) (Found: M^+, 166.1353. $C_{11}H_{18}O$ requires *M*, 166.1358).

(E)-2-*Ethylidene*-6,6-*dimethylcyclohexanone* **62** (R = Me) (78%). R_f (CH_2Cl_2) 0.40; ν_{max}(film)/cm^{-1} 1680 (C=O) and 1620 (C=C); δCDCl$_3$) 6.57 (1 H, qt, *J* 7 and 2, HC=C), 2.46 (2 H, m, CH_2C=C), 1.78–1.60 (7 H, m, CH_2CH_2 and MeC=C) and 1.10 (6 H, s, CMe_2); *m*/*z* 152 (100%, M^+) (Found: M^+, 152.1204. $C_{10}H_{16}O$ requires *M*, 152.1201).

(E)-2-*Benzylidene*-6-*methylcyclohexanone*[43] **61a** (78%).

(E)-6-*Methyl*-2-(2-*methylpropylidene*)*cyclohexanone*[43] **61b** (72%).

(E)-2-*Ethylidene*-4,4-*dimethylcyclohexanone* (81%). R_f-(CH_2Cl_2) 0.38; ν_{max}(film)/cm^{-1} 1680 (C=O) and 1620 (C=C); δ($CDCl_3$) 6.70 (1 H, q, *J* 7, HC=C), 2.42 (2 H, t, *J* 7, CH_2C=O), 2.26 (2 H, s, CH_2C=C), 1.70 (3 H, d, *J* 7, MeC=C), 1.66 (2 H, t, *J* 7, CH_2CH_2C=O) and 1.02 (6 H, s, CMe_2); *m*/*z* 152 (100%, M^+) (Found: M^+, 152.1208. $C_{10}H_{16}O$ requires *M*, 152.1201).

(E)-2-*Benzylidene*-4,4-*dimethylcyclohexanone* (61%). R_f-(CH_2Cl_2) 0.30; ν_{max}(film)/cm^{-1} 1680 (C=O), 1620 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.52 (1 H, t, *J* 2, HC=C), 7.35–7.25 (5 H, m, Ph), 2.63 (2 H, m, CH_2C=C), 2.54 (2 H, t, *J* 7, CH_2CH_2C=O), 1.75 (2 H, t, *J* 7, CH_2CH_2C=O) and 1.02 (6 H, s, Me_2) (Found: M^+, 214.1352. $C_{15}H_{18}O$ requires *M*, 214.1358).

(E)-4,4-*Dimethyl*-2-(2-*methylpropylidene*)*cyclohexanone* (71%). R_f(CH_2Cl_2) 0.36; ν_{max}(film)/cm^{-1} 1680 (C=O) and 1620 (C=C); δ($CDCl_3$) 6.38 (1 H, dt, *J* 9 and 2, HC=C), 2.50 (1 H, m, Me_2CH), 2.41 (2 H, t, *J* 7, CH_2C=O), 2.27 (2 H, m, CH_2C=C), 1.65 (2 H, t, *J* 7, CH_2CH_2C=O), 1.01 (6 H, s, CMe_2) and 0.98 (6 H, d, *J* 7, Me_2CH); *m*/*z* 180 (46%, M^+), 109 (100) (Found: M^+, 180.1517. $C_{12}H_{20}O$ requires *M*, 180.1514).

(E)-4,6-*Dimethylhept*-4-*en*-3-*one*[58] **63** (85%). R_f(CH_2Cl_2) 0.3; ν_{max} 1680 (C=O) and 1620 (C=C); δ($CDCl_3$) 6.37 (1 H, dq, *J* 9 and 1, HC=C), 2.68–2.59 (1 H, m, Me_2CH), 2.64 (2 H, q, *J* 7, $MeCH_2$), 1.75 (3 H, d, *J* 1, MeC=C), 1.05 (3 H, t, *J* 7, $MeCH_2$), 1.00 (6 H, d, *J* 7, Me_2CH); *m*/*z* 140 (50%, M^+) and 111 (100, M − Et) (Found: M^+, 140.1214. $C_9H_{16}O$ requires *M*, 140.1201).

(*E*)-2-*Benzylidene*-5,5-*dimethylcyclopentanone*.—Benzaldehyde (12.0 mmol), 2,2-dimethylcyclopentanone (10.0 mmol) and sodium methoxide (15.0 mmol) were kept in methanol at room temp. for 16 h. The mixture was quenched (HCl, 3 mol dm^{-3}) and extracted with ether. The organic layer was washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (CH_2Cl_2) to give the *ketone* (84%); R_f (CH_2Cl_2) 0.40; ν_{max}(film)/cm^{-1} 1720 (C=O), 1640 (C=C), 1580 and 1500 (Ph); δ($CDCl_3$) 7.6–7.3 (6 H, m, HC=C and Ph), 2.9 (2 H, td, *J* 7 and 3, CH_2CH_2C=C), 1.8 (2 H, t, *J* 7, CH_2CH_2C=C) and 1.1 (6 H, s, CMe_2); *m*/*z* 200 (8%, M^+), 185 (37, M − Me), 116 (100) (Found: M^+, 200.1200. $C_{14}H_{16}O$ requires *M*, 200.1201).

(E)-2-*Benzylidene*-4,4-*dimethylcyclopentanone*.—Benzaldehyde (15.0 mmol) and 3,3-dimethylcyclopentanone (12.0 mmol) were treated similarly with sodium methoxide (20.0 mmol) to give the *ketone* (66%) as prisms, m.p. 66–68 °C (hexane–Et_2O); R_f (CH_2Cl_2) 0.42; ν_{max}(mull)/cm^{-1} 1710 (C=O), 1630 (C=C), 1600 and 1500 (Ph); δ($CDCl_3$) 7.52–7.33 (6 H, m, HC=C and Ph), 2.76 (2 H, d, *J* 2.5, CH_2C=C), 2.25 (2 H, s, CH_2C=O) and 1.12 (6 H, s, CMe_2); *m*/*z* 200 (46%, M^+) and 116 (100) (Found: M^+, 200.1199. $C_{14}H_{16}O$ requires *M*, 200.1201) (Found: C, 83.8; H, 7.9. $C_{14}H_{16}O$ requires C, 83.9; H, 8.0%).

(E)-2-*Benzylidene*-6,6-*dimethylcyclohexanone* **62a**.—The ketone **61a** (13.9 mmol), methyl iodide (28.0 mmol) and potassium *tert*-butoxide (27.9 mmol) in benzene (30 cm^3) were stirred at room temperature for 3 h. The mixture was quenched with aqueous ammonium chloride and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (CH_2Cl_2) to give the ketone (92%) identical (^{1}H NMR and IR) with that reported.[58]

(E)-6,6-*Dimethyl*-2-(2-*methylpropylidene*)*cyclohexanone* **62b**.—The ketone **61b** (20.0 mmol) and LDA (22.0 mmol) were stirred in THF (30 cm^3) at −78 °C for 2 h. Methyl iodide (40.0 mmol) was added to the solution, which was then warmed to 0 °C over 6 h. The mixture was quenched with aqueous ammonium chloride and extracted with ether. The extract was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (CH_2Cl_2) to give the ketone (84%) identical (^{1}H NMR and IR) with that reported.[58]

(E)-2,4,6-*Trimethylhept*-4-*en*-3-*one* **64**.—This was made from **63** by the same method to give the *ketone* (74%); R_f(CH_2Cl_2) 0.30; ν_{max}(film)/cm^{-1} 1685 (C=O) and 1630 (C=C); δ($CDCl_3$) 6.38 (1 H, dq, *J* 9 and 1, HC=C), 3.30 (1 H, septet, *J* 7, Me_2CHC=O), 2.71 (1 H, d septet, *J* 9 and 7, Me_2CHCH), 1.77 (3 H, d, *J* 1, MeC=C), 1.06 (6 H, d, *J* 7, Me_2CH) and 1.04 (6 H, d, *J* 7, Me_2CH); *m*/*z* 154 (28%, M^+), 111 (100, M − Pr^i) (Found: M^+, 154.1356. $C_{10}H_{18}O$ requires *M*, 154.1358).

General Method for the Reduction of Enones to Allylic Alcohols.—Sodium borohydride (7.10 mmol) was added to a stirred mixture of the enone (6.40 mmol) and cerium(III) chloride (7.25 mmol) in methanol (10 cm^3) at 0 °C. After 5 min, the mixture was quenched with aqueous ammonium chloride

and extracted with ether. The ether layer was washed with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (CH_2Cl_2) to give the alcohol. The following allyl alcohols were made by this method.

(E)-2-*Ethylidene*-5,5-*dimethylcyclopentanol* (90%). R_f-(CH_2Cl_2) 0.25; ν_{max} (film)/cm^{-1} 3400 (OH) and 1640 (C=C); δ($CDCl_3$) 5.55–5.30 (1 H, m, HC=C), 3.83 (1 H, s, HCO), 2.30–2.15 (2 H, m, CH_2C=C), 1.60 (3 H, dq, *J* 7 and 1, MeC=C), 1.60–1.31 (3 H, m, CH_2CH$_2$C=C and OH), 0.97 (3 H, s, CMe_AMe$_B$) and 0.81 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 140 (38%, M$^+$) and 55 (100) (Found: M$^+$, 140.1193. $C_9H_{16}O$ requires *M*, 140.1201).

(E)-2-*Ethylidene*-4,4-*dimethylcyclopentanol* (93%). R_f(CH_2Cl_2) 0.24; ν_{max}(film)/cm^{-1} 3350 (OH) and 1640 (C=C); δ($CDCl_3$) 5.6–5.4 (1 H, m, HC=C), 4.5 (1 H, t, *J* 7, C*H*OH), 2.2–2.1 (2 H, m, CH_2C=C), 1.9 (1 H, dd, *J* 12 and 7, CH_AH$_B$CH), 1.7 (1 H, s, OH), 1.6 (3 H, d, *J* 7, MeC=C), 1.5 (1 H, dd, *J* 12 and 7, CH$_A$$H_B$CH), 1.1 (3 H, s, C$Me_AMe_B$) and 0.95 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 140 (40%, M$^+$) and 55 (100) (Found: M$^+$, 140.1197. $C_9H_{16}O$ requires *M*, 140.1203).

(E)-2-*Benzylidene*-5,5-*dimethylcyclopentanol* (92%). R_f-(CH_2Cl_2) 0.20; ν_{max}(mull) 3350 (OH), 1640 (C=C), 1600 and 1500 (Ph); δ($CDCl_3$) 7.5–7.2 (5 H, m, Ph), 6.5 (1 H, q, *J* 2, HC=C), 4.1 (1 H, m, C*H*OH), 2.8–2.5 (2 H, m, CH_2CH_2C=C), 1.8–1.5 (3 H, m, CH_2CH$_2$C=C and OH), 1.1 (3 H, s, CMe_AMe$_B$) and 0.9 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 202 (77, M$^+$), 187 (92, M − Me) and 91 (100, PhCH$_2$) (Found: M$^+$, 202.1357. $C_{14}H_{18}O$ requires *M*, 202.1358).

(E)-2-*Benzylidene*-4,4-*dimethylcyclopentanol* (84%). R_f-(CH_2Cl_2) 0.22; ν_{max}(film)/cm^{-1} 3300 (OH), 1650 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.5–7.2 (5 H, m, Ph), 6.6 (1 H, m, HC=C), 4.7 (1 H, t, *J* 7, C*H*OH), 2.5 (2 H, m, CH_2C=C), 1.9 (1 H, dd, *J* 13 and 7, CH_AH$_B$CHOH), 1.5 (1 H, s, OH), 1.4 (1 H, dd, *J* 13 and 7, CH$_A$$H_B$CHOH), 1.1 (3 H, s, C$Me_AMe_B$) and 0.9 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 202 (56%, M$^+$) and 116 (100) (Found: M$^+$, 202.1358. $C_{14}H_{18}O$ requires *M*, 202.1358).

(E)-5,5-*Dimethyl*-2-(2-*methylpropylidene*)*cyclopentanol* (94%). R_f(CH_2Cl_2) 0.27; ν_{max}(film)/cm^{-1} 3400 (OH) and 1650 (C=C); δ($CDCl_3$) 5.25 (1 H, dq, *J* 9 and 2, HC=C), 3.81 (1 H, s, C*H*OH), 2.35 (1 H, d septet, *J* 9 and 7, Me$_2$C*H*), 2.26–2.14 (2 H, m, CH_2C=C), 1.60–1.30 (3 H, m, CH_2CH$_2$C=C and OH), 0.97 (3 H, s, CMe_AMe$_B$), 0.95 (3 H, d, *J* 7, CHMe_AMe$_B$), 0.94 (3 H, d, *J* 7, CHMe$_A$$Me_B$) and 0.80 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 168 (12%, M$^+$) and 125 (100, M − Pr^i) (Found: M$^+$, 168.1516. $C_{11}H_{20}O$ requires *M*, 168.1514).

(E)-2-(2-*Methylpropylidene*)-4,4-*dimethylcyclopentanol* (97%). R_f(CH_2Cl_2) 0.26; ν_{max}(film)/cm^{-1} 3200 (OH) and 1640 (C=C); δ($CDCl_3$) 5.3 (1 H, dq, *J* 7 and 2, HC=C), 4.5 (1 H, t, *J* *J* 7, C*H*OH), 2.5–2.3 (1 H, m, Me$_2$C*H*), 2.2 (1 H, d, *J* 14, CH$_A$$H_B$C=C), 2.1 (1 H, d, *J* 14, CH_AH$_B$C=C), 1.9 (1 H, dd, *J*13 and 7, CH_AH$_B$CHOH), 1.5 (1 H, s, OH), 1.4 (1 H, dd, *J* 13 and 7, CH$_A$$H_B$CHOH), 1.1 (3 H, s, C$Me_AMe_B$), 1.0 (6 H, d, *J* 7, CHMe_2) and 0.9 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 168 (11%, M$^+$) and 125 (100, M − Pr^i) (Found: M$^+$, 168.1516. $C_{11}H_{20}O$ requires *M*, 168.1514).

(E)-2-*Ethylidene*-6,6-*dimethylcyclohexanol* (90%). R_f-(CH_2Cl_2) 0.26; ν_{max}(film)/cm^{-1} 3400 (OH) and 1660 (C=C); δ($CDCl_3$) 5.37 (1 H, q, *J* 7, HC=C), 3.60 (1 H, s, C*H*OH), 2.29 (1 H, dt, *J* 13 and 6, C=CH_AH$_B$CH$_2$), 2.05 (1 H, dt, *J* 13 and 6, C=CH$_A$$H_BCH_2$), 1.64–1.19 (5 H, m, CH$_2CH_2$ and OH), 1.62 (3 H, d, *J* 7, *Me*CH=C), 0.90 (3 H, s, CMe_AMe$_B$) and 0.86 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 154 (33%, M$^+$) and 83 (100) (Found: M$^+$, 154.1360. $C_{10}H_{18}O$ requires *M*, 154.1357).

(E)-2-*Ethylidene*-4,4-*dimethylcyclohexanol* (88%). R_f-(CH_2Cl_2) 0.23; ν_{max}(film)/cm^{-1} 3350 (OH) and 1660 (C=C); δ($CDCl_3$) 5.55 (1 H, qq, *J* 7 and 1, HC=C), 3.95 (1 H, m, C*H*OH), 2.16 (1 H, br d, *J* 14, CH_AH$_B$C=C), 1.80 (1 H, br d, *J* 14, CH$_A$$H_B$C=C), 1.78–1.32 (5 H, m, CH$_2$CH$_2$ and OH), 1.57 (3 H, d, *J* 7, *Me*CH=C), 0.89 (3 H, s, CMe_AMe$_B$) and 0.87 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 154 (28%, M$^+$) and 111 (100%) (Found: M$^+$, 154.1356. $C_{10}H_{18}O$ requires *M*, 154.1357).

(E)-2-*Benzylidene*-6,6-*dimethylcyclohexanol* (91%). R_f-(CH_2Cl_2) 0.18; ν_{max}(CH_2Cl_2) 3400 (OH), 1650 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.34–7.19 (5 H, m, Ph), 6.46 (1 H, s, HC=C), 3.83 (1 H, s, C*H*OH), 2.59 (1 H, dt, *J* 14 and 6, CH_AH$_B$CH$_2$), 2.17 (1 H, dt, *J* 14 and 6, CH$_A$$H_BCH_2$), 1.70–1.32 (5 H, m, CH$_2CH_2$ and OH), 1.02 (3 H, s, CMe_AMe$_B$) and 0.92 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 216 (100%) (Found: M$^+$, 216.1511. $C_{15}H_{20}O$C requires *M*, 216.1514).

(E)-2-*Benzylidene*-4,4-*dimethylcyclohexanol* (87%). R_f-(CH_2Cl_2) 0.21; ν_{max}(CH_2Cl_2)/cm^{-1} 3350 (OH), 1640 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.39–7.16 (5 H, m, Ph), 6.61 (1 H, s, HC=C), 4.20 (1 H, dd, *J* 6 and 4, C*H*OH), 2.40 (1 H, d, *J* 12, CH_AH$_B$C=C), 1.97 (1 H, d, *J* 12, CH$_A$$H_B$C=C), 1.85–1.42 (5 H, m, CH$_2$CH$_2$ and OH), 1.02 (3 H, s, CMe_AMe$_B$), 0.87 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 216 (100%, M$^+$) and 91 (87, PhCH$_2$) (Found: M$^+$, 216.1493. $C_{15}H_{20}O$ requires *M*, 216.1514).

(E)-6,6-*Dimethyl*-2-(2-*methylpropylidene*)*cyclohexanol* (96%). R_f(CH_2Cl_2) 0.26; ν_{max}(film)/cm^{-1} 3450 (OH); δ($CDCl_3$) 5.12 (1 H, d, *J* 9, HC=C), 3.57 (1 H, s, C*H*OH), 2.57 (1 H, d sextet, *J* 9 and 7, Me$_2$C*H*), 2.30 (1 H, dt, *J* 14 and 7, CH_AH$_B$CH$_2$), 1.98 (1 H, dt, *J* 14 and 7, CH$_A$$H_BCH_2$), 1.66–1.15 (5 H, m, CH$_2CH_2$ and OH), 0.95, (3 H, d, *J* 7, CHMe_AMe$_B$), 0.94 (3 H, d, *J* 7, CHMe$_A$$Me_B$), 0.91 (3 H, s, C$Me_AMe_B$) and 0.85 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 182 (6%, M), 139 (81, M − Pr^i), 126 (82) and 95 (100) (Found: M$^+$, 182.1679. $C_{12}H_{22}O$ requires *M*, 182.1670).

(E)-4,4-*Dimethyl*-2-(2-*methylpropylidene*)*cyclohexanol* (86%). R_f(CH_2Cl_2) 0.24; ν_{max}(film)/cm^{-1} 3300 (OH); δ($CDCl_3$) 5.23 (1 H, d, *J* 9, HC=C), 3.98 (1 H, m, C*H*OH), 2.52 (1 H, d septet, *J* 9 and 7, Me$_2$C*H*), 2.17 (1 H, d, *J* 12, CH_AH$_B$CH$_2$), 1.80 (1 H, d, *J* 12, CH$_A$$H_BCH_2$), 1.84–1.49 (5 H, m, CH$_2CH_2$ and OH), 0.93 (3 H, d, *J* 7, CHMe_AMe$_B$), 0.92 (3 H, d, *J* 7, CHMe$_A$$Me_B$), 0.89 (3 H, s, C$Me_AMe_B$) and 0.87 (3 H, s, CMe$_A$$Me_B$); *m*/*z* 182 (18%, M$^+$), 164 (23, M − H_2O) and 139 (100) (Found: M$^+$, 182.1664. $C_{12}H_{22}O$ requires *M*, 182.1670).

(E)-2,4,6-*Trimethylhept*-4-*en*-3-*ol* (98%). R_f(CH_2Cl_2) 0.25; ν_{max}(film)/cm^{-1} 3500 (OH) and 1630 (C=C); δ($CDCl_3$) 5.15 (1 H, d, *J* 9, HC=C), 3.52 (1 H, d, *J* 8, C*H*OH), 2.52 (1 H, d septet, *J* 9 and 7, Me$_2$C*H*C=C), 1.74 (1 H, septet, *J* 8 and 7, Me$_2$C*H*CHOH), 1.58 (3 H, s, MeC=C), 1.55 (1 H, s, OH), 0.96 (3 H, d, *J* 7, CHMe_AMe$_B$), 0.95 (3 H, d, *J* 7, CHMe_AMe$_B$), 0.92 (3 H, d, *J* 7, CHMe$_A$$Me_B$), 0.76 (3 H, d, *J* 7, CHMe$_A$$Me_B$); *m*/*z* 156 (34%, M$^+$) and 141 (100, M − Me) (Found: M$^+$, 156.1503. $C_{10}H_{20}O$ requires *M*, 156.1514).

Preparation of Propargylic Alcohols.—Typically, butyllithium (1.6 mol dm^{-3} solution in hexane; 12.5 cm^3) was stirred for 10 min with the acetylene (20 mmol) in ether (30 cm^3) under nitrogen at 0 °C. The aldehyde (20 mmol) was added to the mixture, which was then stirred for 2 h. The usual aqueous work-up procedure and distillation gave the alcohols. The following alcohols were prepared by this method.

4-*Phenylbut*-3-*yne*-2-*ol* (73%). B.p. 95–97 °C/3.5 mmHg (lit.,[38] 89–92 °C/3 mmHg); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 4.59 (1 H, q, *J* 7, C*H*OH), 2.45 (1 H, s, OH) and 1.53 (3 H, d, *J* 7, Me).

1-*Phenylbut*-2-*yn*-1-*ol* (86%). B.p. 93–94 °C/0.25 mmHg (lit.,[59] 81 °C/0.2 mmHg); δ($CDCl_3$) 7.5–7.0 (5 H, m, Ph), 5.25 (1 H, q, *J* 2, PhC*H*OH), 4.03 (1 H, s, OH) and 1.80 (3 H, d, *J* 2, Me).

2-*Methylhex*-4-*yn*-3-*ol* (69%). B.p. 65–68 °C/16 mmHg; ν_{max}(film)/cm^{-1} 3421 (OH) and 2220 (C≡C); δ($CDCl_3$) 4.10 (1 H, dq, *J* 5.5 and 2.1, C*H*OH), 2.9 (1 H, s, OH), 2.3–1.5 (1 H, m, C*H*Me$_2$) 1.82 (3 H, d, *J* 2.1, MeC≡C), 0.96 (3 H, d, *J* 6.6, CHMe_AMe$_B$) and 0.94 (3 H, d, *J* 6.6, CHMe$_A$$Me_B$); *m*/*z* 111 (2%, M − H), 97 (24, M − Me) and 69 (100, M − C_6H_7) (Found: M$^+$ − H, 111.0805. $C_7H_{12}O$ requires *M* − H, 111.0810).

5-*Methylhex*-3-*yn*-2-*ol* (81%). B.p. 64–65 °C/18 mmHg; ν_{max}(film)/cm^{-1} 3349 (OH) and 2246 (C≡C); δ($CDCl_3$) 4.46 (1 H, dq, *J* 1.7 and 6.5, C*H*OH), 2.52 (1 H, d septet, *J* 1.7 and 6.8, C*H*Me_2), 2.20 (1 H, s, OH), 1.37 (3 H, d, *J* 6.5, *Me*CHOH), and 1.11 (6 H, d, *J* 6.8, *Me*$_2$CH); *m*/*z* 111 (2%, M − H), 97 (100, M − Me) and 69 (92, M − C_3H_7) (Found: M$^+$ − H, 111.0808. $C_7H_{12}O$ requires *M* − H, 111.0810).

Allylic Alcohols by Grignard Addition to Aldehydes.—Typically, the Grignard reagent (50 mmol) was stirred with the aldehyde (49 mmol) in ether (70 cm^3) for 4 h. The usual aqueous work-up and procedure and distillation gave the allylic alcohols. The following alcohols were prepared by this method.

(E)-1-*Phenylbut*-2-*en*-1-*ol* (75%). B.p. 85–87 °C/1.2 mmHg (lit.,[60] 125–126 °C/15 mmHg).

(E)-4-*Phenylbut*-3-*en*-2-*ol*[61] (85%). ν_{max}(film)/cm^{-1} 3350 (OH); δ($CDCl_3$) 7.4–6.9 (5 H, m, Ph), 6.44 (1 H, d, *J* 15, CH=C*H*Ph), 6.03 (1 H, dd, *J* 15 and 6, C*H*=CHPh), 4.48 (1 H, quintet, *J* 6, C*H*OH), 2.19 (1 H, s, OH) and 1.33 (3 H, d, *J* 6, Me).

(E)-2-*Methylhex*-4-*en*-3-*ol* (75%). B.p. 55–56 °C/17 mmHg (lit.,[62] 55–57 °C/18 mmHg); ν_{max}(film)/cm^{-1} 3370 (OH) and 967 (C=C); δ($CDCl_3$) 5.61 (1 H, dq, *J* 15.4 and 5.4, CH=C*H*Me), 5.36 (1 H, dd, *J* 15.4 and 6.0, C*H*=CHMe), 3.69 (1 H, t, *J* 6.0, C*H*OH), 2.23 (1 H, s, OH), 1.63 (3 H, d, *J* 5.4, C=CMe), 1.62 (1 H, d septet, *J* 6.0 and 6.5, Me_2CH), 0.85 (3 H, d, *J* 6.5, CH$Me_A$$Me_B$) and 0.80 (3 H, d, *J* 6.5, CHMe_B); *m*/*z* 114 (2%, M$^+$) and 71 (100, M − C_3H_7) (Found: M$^+$, 114.1047. $C_7H_{14}O$ requires *M*, 114.1045).

(E)-*Pent*-3-*en*-2-*ol* (78%). B.p. 119–122 °C (lit.,[63] 122 °C); δ($CDCl_3$) 5.9–5.1 (2 H, m, CH=CH), 4.16 (1 H, quintet, *J* 6, C*H*OH), 2.83 (1 H, s, OH), 1.73 (3 H, d, *J* 4, C=CMe), 1.3 (1 H, d, *J* 6, *Me*CHOH).

(E)-5-*Methylhex*-3-*en*-2-*ol*.—5-Methylhex-3-yn-2-ol (2.50 g, 22 mmol) in dry THF (5 cm^3) was added dropwise to a stirred suspension of lithium aluminium hydride (LAH) (1.0 g, 26 mmol) and sodium methoxide (2.0 g, 39 mmol) in dry THF (30 cm^3) at 0 °C and the resulting mixture heated under reflux. After 3 h the mixture was allowed to cool and then cautiously poured into aqueous ammonium chloride (20 cm^3). The resulting slurry was diluted with ether (20 cm^3), filtered through Celite and the Celite pad washed through with ether (20 cm^3). The filtrate was separated and the aqueous phase extracted with ether (3 × 15 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (2.04 g, 80%), b.p. 60–62 °C/16 mmHg; ν_{max}(film)/cm^{-1} 3371 (OH) and 970 (C=C); δ($CDCl_3$) 5.62 (1 H, dd, *J* 15 and 6, C*H*=CH), 5.40 (1 H, dd, *J* 15 and 6, CH=C*H*), 4.22 (1 H, quintet, *J* 6, C*H*OH), 2.25 (1 H, d septet, *J* 6 and 6.5, C*H*Me_2), 1.59 (1 H, s, OH), 1.23 (3 H, d, *J* 6, *Me*CHOH) and 0.97 (6 H, d, *J* 6.5, *Me*$_2$CH); *m*/*z* 114 (2%, M$^+$), 96 (42, M − H_2O), 81 (100, M − H_2O − Me) and 71 (97, M − C_3H_7) (Found: M$^+$, 114.1039. $C_7H_{14}O$ requires *M*, 114.1045).

General Method for the Acylation of Allylic Alcohols.—Typically, the alcohol (10 mmol), acetic anhydride or benzoic anhydride (11 mmol), triethylamine (11 mmol) and DMAP (50 mg, 0.4 mmol) were stirred in dichloromethane (10 cm^3) at room temp. until the reaction was complete (TLC), typically 2–3 h for the acetates and up to 20 h for the benzoates. Ether (50 cm^3) and hydrochloric acid (1 mol dm^{-3} solution; 50 cm^3) were added to the mixture and the organic layer was separated, washed with aqueous sodium hyroxide (1 mol dm^{-3}; 50 cm^3), dried (Na_2SO_4 or $MgSO_4$) and evaporated under reduced pressure. The residue was purified by distillation or flash chromatography (eluting with hexane–Et_2O or CH_2Cl_2), as appropriate. The following propargyl and allyl acetates and benzoates were made by this method.

(E)-*But*-2-*enyl acetate* E-**1a** (86%). B.p. 128–130 °C (lit.,[64] 131 °C); ν_{max}(film)/cm^{-1} 1735 (C=O), 1670 (C=C), and 960 (CH=CH); δ($CDCl_3$) 5.70 (2 H, m, CH=CH), 4.52 (2 H, d, *J* 6.3, CH_2OAc), 2.08 (3 H, s, COMe) and 1.72 (3 H, d, *J* 6.0, MeC=C).

But-2-*ynyl benzoate* (82% *from the alcohol*).[59] R_f(light petroleum–Et_2O, 10:1) 0.32; ν_{max}(film)/cm^{-1} 2261 (C≡C) and 1719 (C=O); δ($CDCl_3$) 8.3–8.0 (2 H, m, *o*-Hs Ph), 7.8–7.3 (3 H, m, *m*- and *p*-Hs Ph), 4.93 (2 H, q, *J* 2.5, CH_2OBz) and 1.93 (3 H, t, *J* 2.5, MeC≡C); *m*/*z* 174 (5%, M$^+$), 105 (100, PhCO) and 77 (19, Ph) (Found: M$^+$, 174.0685. $C_{11}H_{10}O_2$ requires *M*, 174.0681).

(E)-*But*-2-*enyl benzoate* E-**1b** (68%). R_f(light petroleum–Et_2O, 20:1) 0.28; ν_{max}(film)/cm^{-1} 1723 (C=O); δ($CDCl_3$) 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 5.95 (1 H, dt, *J* 15.3 and 5.3, CH=C*H*CHMe), 5.63 (1 H, dq, *J* 15.3 and 4.8, CH=C*H*Me), 4.75 (2 H, dq, *J* 5.2 and 1.1, CH_2OBz) and 1.74 (3 H, dt, *J* 4.8 and 1.1, MeC=C); *m*/*z* 176 (2%, M$^+$), 105 (100, PhCO), 77 (26, Ph) and 55 (21, M − $PhCO_2$) (Found: M$^+$, 176.0850, $C_{11}H_{12}O_2$ requires *M*, 176.0837).

3-*Methylbut*-2-*enyl benzoate* **4** (83%). R_f(light petroleum–Et_2O, 20:1) 0.30; ν_{max}(film)/cm^{-1} 1725 (C=O); δ($CDCl_3$) 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 5.47 (1 H, t septet, *J* 7.4 and 1.4, Me_2C=C*H*), 4.81 (2 H, d, *J* 7.4 H, CH_2OBz) and 1.9–1.7 (6 H, m, Me_2C=C); *m*/*z* 190 (1%, M$^+$), 105 (62, PhCO), 77 (41, Ph) and 68 (100, M − $PhCO_2H$) (Found: M$^+$, 190.1010. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

(E)-*Pent*-3-*en*-2-*yl acetate* E-**7** (81%). B.p. 63–64 °C/50 mmHg (lit.,[65] 50 °C/23 mmHg); ν_{max}(film)/cm^{-1} 1728 (C=O); δ($CDCl_3$) 5.9–4.9 (3 H, m, C*H*=CHCHOAc), 2.03 (3 H, s, MeCO), 1.68 (3 H, d, *J* 5, MeC=C) and 1.28 (3 H, d, *J* 6, *Me*CHOAc).

Pent-3-*yn*-2-*yl acetate* (77%). B.p. 80–82 °C/46 mmHg; ν_{max}(film)/cm^{-1} 2264 (C≡C) and 1737 (C=O); δ($CDCl_3$) 5.39 (1 H, qq, *J* 6.9 and 1.9, C*H*OAc), 2.08 (3 H, s, MeCO), 1.85 (3 H, d, *J* 1.9, MeC≡C) and 1.46 (3 H, d, *J* 6.9, *Me*CHOAc); *m*/*z* 126 (5%, M$^+$), 111 (31, M − Me), 84 (46, M − CH_2CO) and 66 (100, C_5H_6) (Found: M$^+$, 126.0679. $C_7H_{10}O_2$ requires, *M*, 126.0681).

4-*Methylpent*-3-*en*-2-*yl benzoate* **9b** (59%). R_f(light petroleum–Et_2O, 20:1) 0.38; ν_{max}(film)/cm^{-1} 1712 (C=O); δ($CDCl_3$) 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 5.84 (1 H, dq, *J* 8.9 and 6.3, C*H*OBz), 5.28 (1 H, d septet, *J* 8.9 and 1.4, Me_2C=C*H*), 1.77 (3 H, d, *J* 1.4, *Me*$_A$$Me_B$C=C), 1.74 (3 H, d, *J* 1.4, Me_A*Me*$_B$C=C) and 1.39 (3 H, d, *J* 6.3, *Me*CHOBz); *m*/*z* 204 (2%, M$^+$), 105 (97, PhCO), 67 (100, M − $PhCO_2H$ − Me) and 55 (99, M − $PhCO_2$ − C_2H_4) (Found: M$^+$, 204.1147. $C_{13}H_{16}O_2$ requires *M*, 204.1150).

(E)-3-*Methylpent*-3-*en*-2-*yl acetate* **11a**. Methylmagnesium chloride (3 mol dm^{-3} solution in THF; 20.7 cm^3) was added to tiglic aldehyde (4 cm^3, 42 mmol) in THF (10 cm^3) at 0 °C and the mixture stirred for 2 h; an aqueous work-up and acetylation gave the acetate (4.1 g, 70%)], b.p. 158–160 °C; ν_{max}(film)/cm^{-1} 1735 (CO) and 1670 (C=C); δ_H($CDCl_3$) 5.50 (1 H, dq, *J* 1.8 and 6, MeC*H*=), 5.25 (1 H, dq, *J* 6.6, C*H*OAc), 2.02 (3 H, s, COMe), 1.60 (3 H, d, *J* 1.8, CH=C*Me*), 1.58 (3 H, d, *J* 6, C=CH*Me*) and 1.26 (3 H, d, *J* 6.6, *Me*CHOAc); *m*/*z* 142 (10%, M$^+$), 100 (85, M − $COCH_2$), 85 (60, M − $COCH_2$ − Me), 82 (40, M − $COCH_2$ − H_2O) and 67 (100, C_5H_7) (Found: M$^+$, 142.0997. $C_8H_{14}O_2$ requires *M*, 142.0994).

(*E*)-2,4,6-*Trimethylhept*-4-*en*-3-*yl acetate* **11b** (92%). R_f-(CH_2Cl_2) 0.51; ν_{max}(film)/cm^{-1} 1740 (C=O) and 1640 (C=C); δ($CDCl_3$) 5.21 (1 H, d, *J* 9, HC=C), 4.76 (1 H, d, *J* 8, C*H*OAc), 2.49 (1 H, d septet, *J* 9 and 7, Me_2C*H*C=C), 2.03 (3 H, s, MeC=O), 1.88 (1 H, d septet, *J* 8 and 7, Me_2C*H*CHOAc), 1.56 (3 H, s, MeC=C), 0.93 (3 H, d, *J* 7, CH$Me_A$$Me_B$), 0.90 (3 H, d, *J* 7, CH$Me_A$$Me_B$), 0.88 (3 H, d, *J* 7, CHMe_A*Me*$_B$) and 0.78 (3 H, d, *J* 7, CHMe_A*Me*$_B$); *m*/*z* 198 (6%, M$^+$), 156 (28, M − CH_2C=O)

and 113 (100) (Found: M^+, 198.1623. $C_{12}H_{22}O_2$ requires *M*, 198.1620).

Cyclopent-2-enyl acetate **13a** (75%). B.p. 62–63 °C/20 mmHg (lit.,[66] 48 °C/11 mmHg); δ($CDCl_3$) 6.08 (1 H, m, OCHCH=C*H*), 5.79 (1 H, m, OCHC*H*=CH), 5.67 (1 H, m, C*H*OAc), 2.55–1.74 [4 H, m, $(CH_2)_2$] and 2.01 (3 H, s, COMe).

Cyclohex-2-enyl acetate[67] **13b** (88%). R_f(CH_2Cl_2) 0.65; δ($CDCl_3$) 5.92 (1 H, m, OCHCH=C*H*), 5.70 (1 H, m, OCHC*H*=CH), 5.30 (1 H, m, C*H*OAc), 2.10 (3 H, s, COMe) and 1.90–1.40 [6 H, m, $(CH_2)_3$].

2-Methylcyclohex-2-enyl acetate **13c** (62%). B.p. 40–42 °C/1.5 mmHg (lit.,[68] 100 °C/30 mmHg); δ($CDCl_3$) 5.60 (1 H, m, CH=C), 5.15 (1 H, m, C*H*OAc), 2.00 (3 H, s, COMe), 1.80–0.80 [6 H, m, $(CH_2)_3$] and 1.60 (3 H, s, MeC=C).

(E)-*2-Ethylidene-5,5-dimethylcyclopentyl acetate* **15a** (91%). R_f(CH_2Cl_2) 0.47; ν_{max}(film)/cm^{-1} 1740 (C=O) and 1660 (C=C); δ($CDCl_3$) 5.54 (1 H, m, HC=C), 5.10 (1 H, s, C*H*OAc), 2.26–2.21 (2 H, CH_2C=C), 2.07 (3 H, s, MeC=O), 1.67–1.47 (5 H, m, CH_2CH_2C=C and MeC=C), 0.92 (3 H, s, CMe_AMe_B) and 0.90 (3 H, s, CMe_AMe_B); *m*/*z* 182 (31%, M^+) and 140 (100, M − CH_2C=O) (Found: M^+, 182.1298. $C_{11}H_{18}O_2$ requires *M*, 182.1307).

(E)-*2-Benzylidene-5,5-dimethylcyclopentyl acetate* **15b** (95%). R_f(CH_2Cl_2) 0.41; ν_{max}(film)/cm^{-1} 1730 (C=O), 1620 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.57–7.28 (5 H, m, Ph), 6.44 (1 H, t, *J* 3, HC=C), 5.34 (1 H, s, C*H*OAc), 2.90 (2 H, td, *J* 7 and 3, CH_2C=C), 2.13 (3 H, s, MeC=O), 1.85 (2 H, t, *J* 7, CH_2CC=C), 0.99 (3 H, s, CMe_AMe_B) and 0.95 (3 H, s, CMe_AMe_B); *m*/*z* 244 (15%, M^+), 202 (35, M − CH_2C=O) and 91 (100, $PhCH_2$) (Found: M^+, 244.1468. $C_{16}H_{20}O_2$ requires *M*, 244.1463).

(E)-*5,5-Dimethyl-2-(2-methylpropylidene)cyclopentyl acetate* **15c** (90%). R_f(CH_2Cl_2) 0.51; ν_{max}(film)/cm^{-1} 1740 (C=O) and 1640; δ($CDCl_3$) 5.3 (1 H, d, *J* 7, HC=C), 5.1 (1 H, s, C*H*OAc), 2.7–2.2 (3 H, m, Me_2CH and CH_2C=C), 2.1 (3 H, s, MeC=O), 1.8–1.5 (2 H, m, CH_2CH_2=C), 1.1 (6 H, d, *J* 7, Me_2CH), 1.0 (3 H, s, CMe_AMe_B) and 0.9 (3 H, s, CMe_AMe_B); *m*/*z* 210 (34%, M^+) and 168 (100, M − CH_2C=O) (Found: M^+, 210.1628. $C_{13}H_{22}O_2$ requires *M*, 210.1620).

(E)-*2-Ethylidene-6,6-dimethylcyclohexyl acetate* **15d** (85%). R_f(CH_2Cl_2) 0.50; ν_{max}(film)/cm^{-1} 1740 (C=O); δ($CDCl_3$) 5.33 (1 H, q, *J* 7, HC=C), 4.87 (1 H, s, C*H*OAc), 2.21–2.03 (2 H, m, CH_2C=C), 2.06 (3 H, s, MeC=O), 1.70–1.24 (4 H, m, CH_2CH_2C=C), 1.60 (3 H, d, *J* 7, *Me*CH=C), 0.87 (3 H, s, CMe_AMe_B) and 0.84 (3 H, s, CMe_AMe_B); *m*/*z* 181 (16%, M − Me) and 121 (100) (Found: M^+ − Me, 181.1213. $C_{12}H_{20}O_2$ requires *M* − Me, 181.1228).

(E)-*2-Benzylidene-6,6-dimethylcyclohexyl acetate* **15e** (94%). R_f(CH_2Cl_2) 0.43; ν_{max}(film)/cm^{-1} 1740 (C=O), 1660 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.35–7.17 (5 H, m, Ph), 6.37 (1 H, s, HC=C), 5.09 (1 H, s, C*H*OAc), 2.47 (1 H, dt, *J* 13 and 6, CH_AH_BC=C), 2.31 (1 H, dt, *J* 13 and 6, CH_AH_BC=C), 2.13 (3 H, s, MeC=O), 1.69–1.38 (4 H, m, CH_2CH_2), 0.97 (3 H, s, CMe_AMe_B) and 0.93 (3 H, s, CMe_AMe_B); *m*/*z* 258 (6%, M^+), 216 (96, M − CH_2C=O) and 198 (100, M − AcOH) (Found: M^+, 258.1601. $C_{17}H_{22}O_2$ requires *M*, 258.1620).

(E)-*6,6-Dimethyl-2-(2-methylpropylidene)cyclohexyl acetate* **15f** (91%). R_f(CH_2Cl_2) 0.53; ν_{max}(film)/cm^{-1} 1740 (C=O) and 1650 (C=C); δ($CDCl_3$) 5.08 (1 H, dd, *J* 9 and 1, HC=C), 4.85 (1 H, s, C*H*OAc), 2.52 (1 H, d septet, *J* 9 and 7, Me_2CH), 2.23–2.03 (2 H, m, CH_2C=C), 2.07 (3 H, s, MeC=O), 1.63–1.24 (4 H, m, CH_2CH_2), 0.93 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.92 (3 H, d, *J* 7, $CHMe_AMe_B$), 0.87 (3 H, s, CMe_AMe_B) and 0.84 (3 H, s, CMe_AMe_B); *m*/*z* 182 (28%, M − CH_2C=O) and 164 (49, M − AcOH), 139 (100%) (Found: M^+ − CH_2CO, 182.1656. $C_{14}H_{24}O_2$ requires *M* − CH_2CO, 182.1670).

4-Phenylbut-3-yn-2-yl acetate (90%). R_f(hexane–Et_2O, 20:1) 0.2; ν_{max}(film)/cm^{-1} 2247 (C≡C) and 1742 (C=O); δ($CDCl_3$) 7.6–7.1 (5 H, m, Ph), 5.68 (1 H, q, *J* 6.5, C*H*OAc), 2.07 (3 H, s, MeCO) and 1.56 (3 H, d, *J* 6.5, *Me*CHOAc); *m*/*z* 188 (20%, M^+), 173 (18, M − Me), 146 (34, M − CH_2CO) and 128 (100, M − $MeCO_2H$) (Found: M^+, 188.0839. $C_{12}H_{12}O_2$ requires *M*, 188.0837).

4-Phenylbut-3-yn-2-yl benzoate (79%). R_f(hexane–Et_2O, 20:1) 0.36; ν_{max}(film)/cm^{-1} 2251 (C≡C) and 1720 (C=O); δ($CDCl_3$) 8.3–8.1 (2 H, m, *o*-Hs Ph), 7.7–7.2 (8 H, m, *m*- and *p*-Hs Ph), 6.05 (1 H, q, *J* 7, C*H*OBz) and 1.79 (3 H, d, *J* 7, Me); *m*/*z* 250 (24%, M^+), 128 (94, M − BzOH), 105 (100, PhCO) and 77 (44, Ph) (Found: M^+, 250.1000. $C_{17}H_{14}O_2$ requires *M*, 250.0994).

5-Methylhex-3-yn-2-yl acetate (78%). R_f(light petroleum–Et_2O, 20:1) 0.20; ν_{max}(film)/cm^{-1} 2249 (C≡C) and 1741 (C=O); δ($CDCl_3$) 5.43 (1 H, dq, *J* 1.8 and 6.6, C*H*OAc), 2.55 (1 H, d septet, *J* 1.8 and 6.8, C*H*Me_2), 2.03 (3 H, s, MeCO), 1.42 (3 H, d, *J* 6.6, *Me*CHOAc) and 1.13 (6 H, d, *J* 6.8, Me_2CH); *m*/*z* 139 (4%, M − Me), 97 (22, M − CH_2CO − Me) and 87 (100, M − C_5H_7) (Found: M^+, 139.0755. $C_9H_{14}O_2$ requires *M* − Me, 139.0759).

5-Methylhex-3-yn-2-yl benzoate (84%). R_f(hexane–Et_2O, 20:1) 0.3; ν_{max}(film)/cm^{-1} 2258 (C≡C) and 1724 (C=O); δ($CDCl_3$) 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*-and *p*-Hs Ph), 5.70 (1 H, dq, *J* 1.8 and 6.6, C*H*OBz), 2.58 (1 H, d septet, *J* 1.8 and 6.8, C*H*Me_2), 1.57 (3 H, d, *J* 6.6, *Me*CHOBz) and 1.16 (6 H, d, *J* 6.8, Me_2CH); *m*/*z* 216 (13%, M^+), 105 (100, PhCO) and 77 (41, Ph) (Found: M^+, 216.1158. $C_{14}H_{16}O_2$ requires *M*, 216.1150).

(E)-*4-Phenylbut-3-en-2-yl acetate*[20] *E*-**19a** (84%). Acetyl chloride in ether used in place of acetic anhydride.

(E)-*5-Methylhex-3-en-2-yl acetate* E-**19b** (83%). R_f(light petroleum–Et_2O, 20:1) 0.25; ν_{max}(film)/cm^{-1} 1741 (C=O) and 972 (C=C); δ($CDCl_3$) 5.67 (1 H, dd, *J* 15 and 6, CH=C*H*CHOAc), 5.6–5.0 (2 H, m, C*H*=CHOAc), 2.26 (1 H, octet, *J* 6.7, C*H*Me_2), 2.00 (3 H, s, MeCO), 1.26 (3 H, d, *J* 6.3, *Me*CHOAc) and 0.96 (6 H, d, *J* 6.7, Me_2CH); *m*/*z* 156 (2%, M^+), 114 (14, M − CH_2CO), 96 (42, M − AcOH) and 81 (100, M − AcOH − Me) (Found: M^+, 156.1135. $C_9H_{16}O_2$ requires *M*, 156.1150).

(E)-*1-Phenylbut-2-enyl acetate*[20] E-**20a** (88%). Acetyl chloride in ether used in place of acetic anhydride.

(Z)-*1-Phenylbut-2-enyl acetate* Z-**20a** (81%). Acetyl chloride in ether used in place of acetic anhydride; R_f(hexane–Et_2O, 5:1) 0.5; ν_{max}(film)/cm^{-1} 1732 (C=O); δ($CDCl_3$) 7.7–7.3 (5 H, m, Ph), 6.66 (1 H, d, *J* 8.5, PhC*H*), 5.78 (1 H, dq, *J* 12.5 and 6, CH=C*H*Me), 5.70 (1 H, dd, *J* 12.5 and 8.5, C*H*=CHMe), 2.12 (3 H, s, MeCO) and 1.86 (3 H, d, *J* 6, MeC=C); *m*/*z* 190 (14%, M^+), 148 (100, M − CH_2CO), 129 (88, M − AcOH − H), 115 (83, M − AcOH − Me), 105 (81, PhCO) and 91 (80, C_7H_7) (Found: M^+, 190.0984. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

(Z)-*2-Methylhex-4-en-3-yl acetate* E-**20b** (78%). B.p. 67–68 °C/18 mmHg (lit.,[69] 123–126 °C/108 mmHg); R_f(light petroleum–Et_2O, 20:1) 0.25; ν_{max}(film)/cm^{-1} 1731 (C=O) and 969 (CH=CH); δ($CDCl_3$) 5.68 (1 H, dq, *J* 15 and 6, CH=C*H*Me), 5.33 (1 H, ddq, *J* 15, 6.5 and 1, C*H*=CHMe), 4.93 (1 H, t, *J* 6.5, C*H*OAc), 1.98 (3 H, s, MeCO), 1.80 (1 H, octet, *J* 6.5, C*H*Me_2), 1.65 (3 H, dd, *J* 6 and 1, CH=CH*Me*) and 0.84 (6 H, d, *J* 6.5, Me_2CH); *m*/*z* 114 (8%, M − CH_2O), 96 (58, M − AcOH) and 81 (100, M − AcOH − Me) (Found: M^+ − CH_2O, 114.1051. $C_9H_{16}O_2$ requires *M* − CH_2O, 114.1045).

2-Methylhex-4-yn-3-yl acetate (81%). B.p. 84–86 °C/16 mmHg; ν_{max}(film)/cm^{-1} 2248 (C≡C) and 1743 (C=O); δ($CDCl_3$) 5.16 (1 H, dq, *J* 5.6 and 2.2, C*H*OAc), 2.3–1.5 (1 H, m, C*H*Me_2), 2.05 (3 H, s, MeCO), 1.83 (3 H, d, *J* 2.2, MeC≡C), 0.98 (3 H, d, *J* 6.7, $CHMe_AMe_B$) and 0.95 (3 H, d, *J* 6.7, $CHMe_AMe_B$); *m*/*z* 154 (9%, M^+), 139 (69, M − Me), 112 (65, M − CH_2CO), 111 (70, M − C_3H_7), 94 (68, M − AcOH) and 79 (100, M − AcOH − Me) (Found: M^+, 154.0993. $C_9H_{14}O_2$ requires *M*, 154.0994).

(E)-4-*Trimethylsilylbut*-3-*en*-2-*yl benzoate* E-**40b** (84%). Benzoyl chloride used in place of benzoic anhydride; R_f(hexane–Et_2O, 20:1) 0.25; ν_{max}(film)/cm^{-1} 1719 (C=O); δ($CDCl_3$) 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 6.16 (1 H, dd, *J* 18.8 and 3.9, C*H*=CHSi), 5.93 (1 H, d, *J* 18.8, CH=C*H*Si), 5.59 (1 H, dq, *J* 3.9 and 6.5, C*H*OBz), 1.42 (3 H, d, *J* 6.5, *Me*CHOBz) and 0.76 (9 H, s, $SiMe_3$); *m*/*z* 248 (1%, M$^+$), 143 (16, M – PhCO), 105 (100, PhCO) and 73 (48, $SiMe_3$) (Found: M$^+$, 248.1241. $C_{14}H_{202}Si$ requires *M*, 248.1232).

4-*Trimethylsilylbut*-3-*yn*-2-*yl benzoate* (91%). Benzoyl-chloride used in place of benzoic anhydride; R_f(hexane–Et_2O, 20:1) 0.31; ν_{max}(film)/cm^{-1} 2203 (C≡C) and 1712 (C=O); δ($CDCl_3$) 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.3 (3 H, m, *m*- and *p*-Hs Ph), 5.63 (1 H, q, *J* 6.7, C*H*OBz), 1.60 (3 H, d, *J* 6.7, *Me*CHOBz) and 0.17 (9 H, s, $SiMe_3$); *m*/*z* 246 (95%, M$^+$), 231 (21, M – Me), 141 (100, M – PhCO) and 105 (67, PhCO) (Found: M$^+$, 246.1078. $C_{14}H_{18}O_2Si$ requires *M*, 246.1076).

cis-5-*Methylcyclohex*-2-*enyl benzoate* **48** (76%). R_f(hexane–Et_2O, 20:1) 0.4; ν_{max}(film)/cm^{-1} 1725 (C=O); δ($CDCl_3$) 8.1–8.0 (2 H, m, *o*-Hs Ph), 7.6–7.2 (3 H, m, *m*- and *p*-Hs Ph), 5.88 (1 H, ddd, *J* 10.0, 4.7 and 2.6, C*H*=CHCOBz), 5.71 (1 H, ddd, *J* 10.0, 2.7 and 1.7, CH=C*H*COBz), 5.63 (1 H, m, C*H*OBz), 2.3–2.0 (2 H, m, equatorial Hs), 1.88 (1 H, m, C*H*Me), 1.73 (1 H, m, C=CCH_AH_B), 1.41 (1 H, td, *J* 12.0 and 9.8, CH_AH_BCOBz *cis* to Me) and 1.02 (3 H, d, *J* 6.5, Me); *m*/*z* 216 (5%, M$^+$), 160 (7, M – C_4H_8) and 105 (100, PhCO) (Found: M$^+$, 216.1138. $C_{14}H_{16}O_2$ requires *M*, 216.1150).

(E)-4-*Phenylbut*-3-*en*-2-*yl Methanesulfonate*.—Methanesulfonyl chloride (0.39 g) was stirred with the alcohol (0.5 g) and triethylamine (0.4 g) in dry ether (25 cm^3) at 0 °C for 2 h at room temp. The mixture was filtered and the filtrate evaporated under reduced pressure to give the *mesylate* (0.59 g, 77%); ν_{max}(film)/cm^{-1} 1397, 1192 (SO_2) and 966 (C=C); δ($CDCl_3$) 7.6–7.0 (5 H, m, Ph), 6.45 (1 H, d, *J* 16, PhC*H*), 6.05 (1 H, dd, *J* 16 and 6, PhCH=C*H*), 4.58 (1 H, quintet, *J* 6, C*H*OMs), 2.72 (3 H, s, $MeSO_2$) and 1.65 (3 H, d, *J* 6, *Me*CHOMs).

General Method for the Preparation of Allylic N-*Phenylcarbamates*.—Typically, phenyl isocyanate (4.0 g, 34 mmol) was kept with the alcohol (33 mmol), DMAP (4.4 g, 36 mmol) and triethylamine (4.0 g, 40 mmol) in dry dichloromethane (30 cm^3) under nitrogen at room temp. for 3 h. The mixture was filtered and evaporated under reduced pressure, and the residue chromatographed (hexane–Et_2O, 5:1, or CH_2Cl_2) to give the carbamate. The following allyl carbamates were made by this method.

(E)-2-*Ethylidene*-4,4-*dimethylcyclopentyl* N-*phenylcarbamate* **23a** (69%). R_f(CH_2Cl_2) 0.52; ν_{max}(CH_2Cl_2)/cm^{-1} 3300 (NH), 1690 (C=O), 1620 (C=C), 1600 and 1500 (Ph); δ($CDCl_3$) 7.40–7.01 (5 H, m, Ph), 6.61 (1 H, s, NH), 5.70 (1 H, qq, *J* 7 and 2, HC=C), 5.54 (1 H, td, *J* 6 and 2, CHO), 2.19–2.13 (2 H, m, CH_2C=C), 2.00 (1 H, dd, *J* 13 and 6, CH_AH_BCHO), 1.64 (3 H, d, *J* 7, MeCH), 1.62 (1 H, dd, *J* 13 and 6, CH_AH_BCHO), 1.12 (3 H, s, CMe_AMe$_B$) and 1.00 (3 H, s, CMe$_A$*Me*$_B$); *m*/*z* 259 (7%, M$^+$), 215 (59, M – CO_2) and 123 (100, M – PhNHCO$_2$) (Found: M$^+$, 259.1570. $C_{16}H_{21}NO_2$ requires *M*, 259.1572).

(E)-2-*Benzylidene*-4,4-*dimethylcyclopentyl* N-*phenylcarbamate* **23b** (65%). Prisms, m.p. 83–84 °C (from EtOH–H_2O); R_f(CH_2Cl_2) 0.50; ν_{max}(mull)/cm^{-1} 3400 (NH), 1710 (C=O), 1670 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.50–7.04 (10 H, m, Ph), 6.70 (1 H, s, NH), 6.65 (1 H, q, *J* 2, HC=C), 5.80 (1 H, t, *J* 7, CHO), 2.54 (2 H, m, CH_2C=C), 2.10 (1 H, dd, *J* 12 and 7, CH_AH_BCHO), 1.70 (1 H, dd, *J* 12 and 7, CH$_A$*H*$_B$CHO), 1.17 (3 H, s, CMe_AMe$_B$) and 1.03 (3 H, s, CMe$_A$*Me*$_B$); *m*/*z* 277 (7%, M$^+$ – CO_2), 185 (100, M – PhNHCO$_2$) and 91 (74, $PhCH_2$) (Found: M$^+$ – CO_2, 277.1850. $C_{21}H_{23}NO_2$ requires *M* – CO_2, 277.1831) (Found: C, 78.7; H, 6.8; N, 4.2. $C_{21}H_{23}NO_2$ requires C, 78.5; H, 7.2; N, 4.4%).

(E)-4,4-*Dimethyl*-2-(2-*methylpropylidene*)*cyclopentyl* N-*phenylcarbamate* **23c** (87%). As prisms, m.p. 73–75 °C (from EtOH–H_2O); R_f(CH_2Cl_2) 0.60; ν_{max}(mull)/cm^{-1} 3300 (NH), 1690 (C=O), 1600 and 1500 (Ph); δ($CDCl_3$) 7.40–7.03 (5 H, m, Ph), 6.63 (1 H, s, NH), 5.54 (1 H, t, *J* 7, CHO), 5.43 (1 H, d, *J* 9, HC=C), 2.35 (1 H, d septet, *J* 9 and 7, Me_2CHC=C), 2.20 (1 H, d, *J* 15, CH_AH_BC=C), 2.14 (1 H, d, *J* 15, CH$_A$*H*$_B$C=C), 1.99 (1 H, dd, *J* 13 and 7, CH_AH_BCHO), 1.58 (1 H, dd, *J* 13 and 7, CH$_A$*H*$_B$CHO), 1.11 (3 H, s, CMe_AMe$_B$), 1.00 (3 H, s, CMe$_A$*Me*$_B$) and 0.96 (6 H, d, *J* 7, *Me*$_2$CH); *m*/*z* 287 (5%, M$^+$) and 151 (100, M – PhNHCO$_2$) (Found: M$^+$, 287.1884. $C_{18}H_{25}NO_2$ requires *M*, 287.1885) (Found: C, 75.2; H, 8.9; N, 5.0. $C_{18}H_{25}NO_2$ requires C, 75.2; H, 8.8; N, 4.9%).

(E)-2-*Ethylidene*-4,4-*dimethylcyclohexyl* N-*phenylcarbamate* **23d** (85%). R_f(CH_2Cl_2) 0.45; ν_{max}(CH_2Cl_2)/cm^{-1} 3300 (NH), 1680 (C=O), 1630 (C=C), 1600 and 1500 (Ph); δ($CDCl_3$) 7.50–7.02 (5 H, m, Ph), 6.55 (1 H, s, NH), 5.62 (1 H, q, *J* 7, HC=C), 5.16 (1 H, dd, *J* 5 and 4, CHO), 2.04 (2 H, s, CH_2C=C), 1.94–1.25 (4 H, m, CH_2CH_2), 1.59 (3 H, d, *J* 7, *Me*CH=C), 0.97 (3 H, s, CMe_AMe$_B$) and 0.89 (3 H, s, CMe$_A$*Me*$_B$); *m*/*z* 273 (6%, M$^+$), 229 (18, M – CO_2) and 137 (100, M – PhNHCO$_2$) (Found: M$^+$, 273.1719. $C_{17}H_{23}NO_2$ requires *M*, 273.1729).

(E)-2-*Benzylidene*-4,4-*dimethylcyclohexyl* N-*phenylcarbamate* **23e** (72%). R_f(CH_2Cl_2) 0.63; ν_{max}(CH_2Cl_2)/cm^{-1} 3300 (NH), 1680 (C=O), 1620 (C=C), 1600, 1580 and 1500 (Ph); δ($CDCl_3$) 7.42–7.02 (10 H, m, Ph), 6.70–6.63 (2 H, m, HC=C and NH), 5.31 (1 H, t, *J* 5, CHO), 2.30 (1 H, d, *J* 14, CH_AH_BC=C), 2.17 (1 H, d, *J* 14, CH$_A$*H*$_B$C=C), 2.01–1.33 (4 H, m, CH_2CH_2), 0.93 (3 H, s, CMe_AMe$_B$) and 0.89 (3 H, s, CMe$_A$*Me*$_B$); *m*/*z* 291 (7%, M – CO_2) and 200 (100, M – PhNHCO$_2$) (Found: M$^+$ – CO_2, 291.1994. $C_{22}H_{25}NO_2$ requires *M* – CO_2, 291.1987).

(E)-2-(2-*Methylpropylidene*)-4,4-*dimethylcyclohexyl* N-*phenylcarbamate* **23f** (88%). R_f(CH_2Cl_2) 0.48; ν_{max}(film)/cm^{-1} 3300 (NH), 1680 (C=O), 1620 (C=C), 1600 and 1500 (Ph); δ-($CDCl_3$) 7.48–6.95 (5 H, m, Ph), 6.55 (1 H, s, NH), 5.33 (1 H, d, *J* 8, HC=C), 5.12 (1 H, t, *J* 4, CHO), 2.55 (1 H, d septet, *J* 8 and 6, Me_2CH), 2.04 (2 H, m, CH_2C=C), 1.93–1.22 (4 H, m, CH_2CH_2), 0.99 (3 H, s, CMe_AMe$_B$), 0.94 (6 H, d, *J* 6, CH*Me*$_2$) and 0.89 (3 H, s, CMe$_A$*Me*$_B$); *m*/*z* 257 (4%, M – CO_2) and 165 (100, M – PhNHCO$_2$) (Found: M$^+$ – CO_2, 257.2157. $C_{19}H_{27}NO_2$ requires *M* – CO_2, 257.2143).

(E)-2-*Ethylidenecyclohexyl* N-*phenylcarbamate* **25** (89%). R_f-(CH_2Cl_2) 0.52; ν_{max}(film)/cm^{-1} 3300 (NH), 1695 (CO) and 1603 (Ph); δ_H($CDCl_3$) 7.40–7.25 (4 H, m, *o*- and *m*-Ph), 7.07–7.00 (1 H, m, *p*-Ph), 6.58 (1 H, s, NH), 5.50 (1 H, qd, *J* 6.8 and 0.9, C=CH), 5.20 (1 H, m, CHO), 2.30–2.20 (2 H, m, ring Hs), 1.85–1.40 (6 H, m, ring Hs) and 1.161 (3 H, d, *J* 6.8, CH*Me*); δ_C($CDCl_3$) 153.0, 138.0, 136.8, 128.8, 122.9, 118.6, 76.7, 33.0, 26.5, 25.2, 22.3 and 12.3; *m*/*z* 245 (1%, M$^+$), 201 (6, M – CO_2), 186 (7, M – CO_2 – Me), 109 (100, M – PhNHCO$_2$) and 93 ($PhNH_2$) (Found: M$^+$, 245.1425. $C_{15}H_{19}NO_2$ requires *M*, 245.1415).

1-(*Cyclohexenyl*)*ethyl* N-*phenylcarbamate* **27**. 1-Acetylcyclohexene was reduced in the usual way and the crude alcohol converted directly to the *carbamate* (98%); R_f(CH_2Cl_2) 0.50; ν_{max}(film)/cm^{-1} 3300 (NH), 1700 (CO) and 1605 (Ph); δ_H($CDCl_3$) 7.40–7.00 (5 H, m, Ph), 6.56 (1 H, s, NH), 5.74 (1 H, m, C=CH), 5.24 (1 H, q, *J* 6.5, CHO), 2.05–2.01 (4 H, m, CH_2C=CHCH_2), 1.67–1.52 (4 H, m, CH_2CH_2) and 1.35 (3 H, d, *J* 6.5, CH*Me*); δ_C($CDCl_3$) 153.1, 138.1, 137.0, 128.8, 123.6, 123.0, 118.5, 75.0, 24.7, 24.0, 22.3, 22.2 and 18.9; *m*/*z* 245 (1.6%, M$^+$), 201 (6, M – CO_2), 186 (5, M – CO_2 – Me), 109 (100, M – PhNHCO$_2$) and 93 (50, $PhNH_2$) (Found: M$^+$, 245.1406. $C_{15}H_{19}NO_2$ requires *M*, 245.1415).

4-*Phenylbut*-3-*yn*-2-*yl* N-*phenylcarbamate* (82%). Needles,

m.p. 64–65 °C (from hexane); R_f(hexane–Et_2O, 5:1) 0.4; ν_{max}-(CH_2Cl_2)/cm^{-1} 3410 (NH), 2254 (C≡C) and 1731 C=O); δ($CDCl_3$) 7.6–6.9 (10 H, m, 2 × Ph), 6.68 (1 H, s, NH), 5.75 (1 H, q, *J* 6.6, CHO) and 1.64 (3 H, d, *J* 6.6, Me); *m*/*z* 265 (3%, M^+), 129 (100, M − $PhNHCO_2$) and 93 (16, $PhNH_2$) (Found: C, 77.3; H, 5.65; N, 5.3. $C_{17}H_{15}NO_2$ requires C, 77.0; H, 5.65; N, 5.3%).

(E)-4-*Phenylbut*-3-*en*-2-*yl* N-*phenylcarbamate* E-**29a** (83%). Needles, m.p. 86–87 °C (from hexane–EtOAc); R_f(hexane–Et_2O, 10:1) 0.22; ν_{max}(CH_2Cl_2)/cm^{-1} 3409 (NH) and 1727 (C=O); δ($CDCl_3$) 7.5–6.9 (10 H, m, 2 × Ph), 6.68 (1 H, d, *J* 15.9, PhC*H*=CH), 6.58 (1 H, s, NH), 6.21 (1 H, dd, *J* 15.9 and 6.4, PhCH=C*H*), 5.54 (1 H, quintet, *J* 6.4, CHO) and 1.48 (3 H, d, *J* 6.4, Me); *m*/*z* 267 (1%, M^+), 131 (100, M − $PhNHCO_2$) and 91 (41, C_7H_7) (Found: C, 76.2; H, 6.30; N, 5.2. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.35; N, 5.2%).

(E)-5-*Methylhex*-3-*en*-2-*yl* N-*phenylcarbamate* E-**29b** (85%). R_f(hexane–Et_2O, 5:1) 0.3; ν_{max}(film)/cm^{-1} 3324 (NH), 1693 (C=O) and 972 (C=C); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 5.60 (1 H, s, NH), 5.76 (1 H, dd, *J* 15 and 6, CH=C*H*CHO), 5.7–5.1 (2 H, m, C*H*=CHCHO), 2.30 (1 H, octet, *J* 6.7, C*H*Me_2), 1.35 (3 H, d, *J* 6.3, MeCO) and 1.00 (6 H, d, *J* 6.7, *Me*$_2$CH); *m*/*z* 233 (11, M^+), 97 (41, M − $PhNHCO_2$) and 55 (100, C_4H_7) (Found: M^+, 233.1428. $C_{14}H_{19}NO_2$ requires *M*, 233.1416).

(E)-*Pent*-3-*en*-2-*yl* N-*phenylcarbamate* E-**29c** (78%). Needles, m.p. 34–36 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3412 (NH) and 1727 (C=O); δ ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.56 (1 H, s, NH), 6.0–5.1 (3 H, m, CH=CHCHO), 1.71 (3 H, d, *J* 5.3, MeC=C) and 1.35 (3 H, d, *J* 6.3, *Me*CHO); *m*/*z* 205 (6%, M^+), 93 (39, $PhNH_2$) and 69 (100, M − $PhNHCO_2$) (Found: C, 70.3; H, 7.35; N, 6.8. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.30; N, 6.8%).

(E)-2-*Methylhex*-4-*en*-3-*yl* N-*phenylcarbamate* E-**30b** (78%). As an amorphous solid, m.p. 64–65 °C (from hexane); ν_{max}-(Nujol)/cm^{-1} 3325 (NH) and 1692 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.55 (1 H, s, NH), 5.79 (1 H, dq, *J* 15 and 6, CH=C*H*Me), 5.41 (1 H, ddq, *J* 15, 7 and 1, C*H*=CHMe), 4.97 (1 H, t, *J* 6.5, CHO), 1.90 (1 H, octet, *J* 6.5, C*H*Me), 1.72 (3 H, dd, *J* 6 and 1, MeC=C), 0.94 (3 H, d, *J* 6.5, CH*Me*$_A$Me$_B$) and 0.92 (3 H, d, *J* 6.5, CHMe$_A$*Me*$_B$); *m*/*z* 233 (7%, M^+), 97 (77, M − $PhNHCO_2$) and 55 (100, C_4H_7) (Found: M^+, 233.1412. $C_{14}H_{19}NO_2$ requires *M*, 233.1416).

1-*Phenylbut*-2-*ynyl* N-*phenylcarbamate* (87%). Needles, m.p. 98–99 °C (from hexane); R_f(hexane–Et_2O, 5:1) 0.4; ν_{max}-(CH_2Cl_2)/cm^{-1} 3407 (NH), 2256 (C≡C) and 1728 (C=O); δ($CDCl_3$) 7.7–6.9 (10 H, m, 2 × Ph), 6.66 (1 H, s, NH), 6.48 (1 H, q, *J* 2.2, PhC*H*) and 1.92 (3 H, d, *J* 2.2, Me); *m*/*z* 262 (5%, M^+), 221 (26, M − CO_2) and 129 (100, M − $PhNHCO_2$) (Found: C, 76.9; H, 5.75; N, 5.3. $C_{17}H_{15}NO_2$ requires C, 77.0; H, 5.65; N, 5.3%).

5-*Methylhex*-3-*yn*-2-*yl* N-*phenylcarbamate* (90%). An amorphous solid, m.p. 55–56 °C; R_f(hexane–Et_2O, 5:1) 0.3; ν_{max}-(Nujol)/cm^{-1} 3326 (NH), 2249 (C≡C) and 1700 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.65 (1 H, s, NH), 5.51 (1 H, dq, *J* 1.8 and 6.6, CHO), 2.58 (1 H, d septet, *J* 1.8 and 6.8, C*H*Me_2), 1.51 (3 H, d, *J* 6.6, *Me*CHO) and 1.16 (6 H, d, *J* 6.8, *Me*$_2$CH); *m*/*z* 231 (16%, M^+), 95 (31, M − $PhNHCO_2$), 93 (39, $PhNH_2$) and 55 (100, C_4H_7) (Found: M^+, 231.1252. $C_{14}H_{17}NO_2$ requires *M*, 231.1259).

2-*Methylhex*-4-*yn*-3-*yl* N-*phenylcarbamate* (74%). R_f(hexane–Et_2O, 5:1) 0.3; ν_{max}(film)/cm^{-1} 3320 (NH), 2237 (C≡C) and 1704 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.62 (1 H, s, NH), 5.23 (1 H, dq, *J* 5.5 and 2.2, CHO), 1.98 (1 H, d septet, *J* 5.5 and 6.7, C*H*Me_2), 1.86 (3 H, d, *J* 2.2, MeC≡C), 1.04 (3 H, d, *J* 6.7, CH*Me*$_A$Me$_B$) and 1.01 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$); *m*/*z* 231 (41%, M^+), 144 (36, M − CO_2 − C_3H_7), 95 (100, M − $PhNHCO_2$) and 93 (89, $PhNH_2$) (Found: M^+, 231.1264. $C_{14}H_{17}NO_2$ requires *M*, 231.1259).

But-2-*ynyl* N-*phenylcarbamate* (85%). Needles, m.p. 64–66 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3503, 3407 (NH), 2257 (C≡C) and 1739 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.82 (1 H, s, NH), 4.75 (2 H, q, *J* 2.5, CH_2O) and 1.83 (3 H, t, *J* 2.5, MeC≡C); *m*/*z* 189 (90%, M^+), 144 (30, M − CO_2H), 93 (40, $PhNH_2$) and 53 (100, M − $PhNHCO_2$) (Found: C, 69.8; H, 5.85; N, 7.2. $C_{11}H_{11}NO_2$ requires C, 69.8; H, 5.80; N, 7.4%).

(E)-*But*-2-*enyl* N-*phenylcarbamate* E-**35** (88%). Needles, m.p. 70–72 °C (from hexane); ν_{max}(CH_2Cl_2)cm^{-1} 3415 (NH) and 1727 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.68 (1 H, s, NH), 5.91 (1 H, dt, *J* 15.2 and 5.5. C*H*=CHMe), 5.56 (1 H, dq, *J* 15.2 and 5.1, CH=C*H*Me), 4.59 (2 H, dq, *J* 5.5 and 1.0, CH_2O) and 1.73 (3 H, dt, *J* 5.1 and 1.0, MeC=C); *m*/*z* 191 (14%, M^+), 132 (12, M − CO_2 − Me), 93 (24, $PhNH_2$) and 55 (100, M − $PhNHCO_2$) (Found: C, 69.1; H, 7.10; N, 7.2. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.80; N, 7.3%).

3-*Methylbut*-2-*enyl* N-*phenylcarbamate* **36** (79%). Needles, m.p. 63–65 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3410 (NH) and 1720 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.63 (1 H, s, NH), 5.40 (1 H, t septet, *J* 5.9 and 1.4, Me_2C=C*H*), 4.66 (2 H, d, *J* 5.9, CH_2O) and 1.85–1.65 (6 H, m, Me_2C=C); *m*/*z* 205 (24%, M^+), 93 (71, $PhNH_2$), 69 (100, M − $PhNHCO_2$) and 41 (83, C_3H_5) (Found: C, 70.2; H, 7.40; N, 6.9. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.30; N, 6.8%).

4-*Methylpent*-3-*en*-2-*yl* N-*phenylcarbamate* **38** (86%). As prisms, m.p. 63–64 °C (pentane); R_f(CH_2Cl_2) 0.71; ν_{max}-($CDCl_3$)/cm^{-1} 3420 (NH), 1715 (CO) and 1600 (Ph); δ_H-($CDCl_3$) 7.50–7.10 (5 H, m, Ph), 6.60 (1 H, s, NH), 5.60 (1 H, dq, *J* 8.8 and 6.3, MeC*H*O), 5.21 (1 H, d septet, *J* 8.8 and 1.6, Me_2C=C*H*), 1.75 (3 H, d, *J* 1.6, *Me*$_A$Me$_B$C=C), 1.73 (3 H, d, *J* 1.6, Me$_A$*Me*$_B$C=C) and 1.33 (3 H, d, *J* 6.3, *Me*CHO); δ_C($CDCl_3$) 153.1, 138.1, 136.5, 128.9, 124.9, 123.1, 118.5, 69.1, 25.6, 21.1 and 18.3; *m*/*z* 219 (1%, M^+), 175 (3, M − CO_2), 160 (3, M − CO_2 − Me), 93 (70, $PhNH_2$) and 83 (100, M − $PhNHCO_2$) (Found: M^+, 219.1263. $C_{13}H_{17}NO_2$ requires *M*, 219.1259) (Found: C, 71.3; H, 8.05; N, 6.4. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.80; N, 6.2%).

(E)-4-*Trimethylsilylbut*-3-*en*-2-*yl* N-*phenylcarbamate* E-**40a** (79%). Needles, m.p. 57–58 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3405 (NH) and 1725 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.57 (1 H, s, NH), 6.13 (1 H, dd, *J* 18.7 and 3.5, C*H*=CHSi), 5.74 (1 H, d, *J* 18.7, CH=C*H*Si), 5.35 (1 H, dq, *J* 3.5 and 6.5, CHO), 1.35 (3 H, d, *J* 6.5, *Me*CHO) and 0.08 (9 H, s, $SiMe_3$); *m*/*z* 263 (4%, M^+), 127 (60, M − $PhNHCO_2$), 99 (69, CH=CHSiMe_3), 93 (55, $PhNH_2$) and 73 (100, $SiMe_3$) (Found: C, 63.6; H, 8.00; N, 5.1. $C_{14}H_{21}NO_2Si$ requires C, 63.9; H, 8.00; N, 5.3%).

4-*Trimethylsilylbut*-3-*yn*-2-*yl* N-*phenylcarbamate* (82%). Needles, m.p. 88–90 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3407 (NH) and 1728 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.60 (1 H, s, NH), 5.52 (1 H, q, *J* 6.7, CHO), 1.53 (3 H, d, *J* 6.7, *Me*CHO) and 0.18 (9 H, s, $SiMe_3$); *m*/*z* 261 (47%, M^+), 202 (35, M − CO_2NH), 125 (95, M − $PhNHCO_2$), 97 (100, C≡CSiMe_3) and 93 (63, $PhNH_2$) (Found: C, 64.6; H, 7.35; N, 5.6. $C_{14}H_{19}NO_2Si$ requires C, 64.4; H, 7.30; N, 5.4%).

2-*Methyl*-4-*trimethylsilylbut*-3-*yn*-2-*yl* N-*phenylcarbamate* (73%). Needles, m.p. 147–148 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3407 (NH) and 1728 (C=O); δ($CDCl_3$) 7.6–6.9 (5 H, m, Ph), 6.59 (1 H, s, NH), 1.69 (6 H, s, Me_2CO) and 0.09 (9 H, s, $SiMe_3$); *m*/*z* 275 (13%, M^+), 139 (73, M − $PhNHCO_2$), 97 (99, C≡C$SiMe_3$) and 93 (100, $PhNH_2$) (Found: C, 65.2; H, 7.65; N, 5.0. $C_{15}H_{21}NO_2Si$ requires C, 65.5; H, 7.65; N, 5.1%).

cis-5-*Methylcyclohex*-2-*enyl* N-*phenylcarbamate* **46** (81%). Needles, m.p. 88–89 °C (lit.,[26] 91.5–92.5 °C) (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3410 (NH) and 1723 (C=O); δ($CDCl_3$) 7.4–7.0 (5 H, m, Ph), 6.56 (1 H, s, NH), 5.85 (1 H, ddd, *J* 9.8, 4.9 and 2.5, C*H*=CHCO), 5.66 (1 H, d, *J* 9.8, CH=C*H*CO), 5.38 (1 H, m, CHO), 2.2–2.0 (2 H, m, equatorial Hs), 1.83 (1 H, m, MeC*H*), 1.67 (1 H, m, C=CCH_AH$_B$ *cis* to Me), 1.29 (1 H, dt, *J* 10.1 and

12.1, CH_AH_BCOR *cis* to Me) and 0.99 (3 H, d, *J* 6.4, Me); *m/z* 231 (3%, M^+), 187 (3, M − CO_2), 95 (92, M − $PhNHCO_2$) and 93 (100, $PhNH_2$) (Found: C, 72.5; H, 7.35; N, 6.0. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.35; N, 6.1%).

Hydrogenation of Propargylic Alcohol Derivatives.—Typically the palladium catalyst (5% on $BaSO_4$, 0.1 g) in methanol (15 cm^3) was stirred under hydrogen at 1 atm for 0.5 h. The acetate, benzoate or carbamate (1.0 g) and quinoline (0.3 g) were added and stirring under hydrogen continued for 1.5 h. The catalyst was filtered off and the filtrate evaporated under reduced pressure. The residue was chromatographed (hexane–Et_2O, 10:1) to give the acetate, benzoate or carbamate. The following (*Z*)-allylic alcohol derivatives were prepared by this method.

(Z)-*But*-2-*enyl benzoate* Z-**1b** (81% *as an* 86:14 *mixture of* Z- *and* E-*isomers*. R_f(light petroleum–Et_2O, 10:1) 0.38; ν_{max}(film)/ cm^{-1} 1722 (C=O); $\delta(CDCl_3)$ 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 6.1–5.4 (2 H, m, CH=CH), 4.89 (2 H, dq, *J* 5.2 and 0.8, CH_2O) and 1.76 (3 H, dt, *J* 5.2 and 0.8, MeC=C); *m/z* 176 (1%, M^+), 105 (100, PhCO), 77 (33, Ph) and 55 (29, M − $PhCO_2$) (Found: M^+, 176.0824. $C_{11}H_{12}O_2$ requires *M*, 176.0837).

(Z)-*Pent*-3-*en*-2-*yl acetate* Z-**7** (58%). B.p. 62–64 °C/44 mmHg; ν_{max}(film)/cm^{-1} 1731 (C=O); $\delta(CDCl_3)$ 5.9–5.1 (3 H, m, C*H*=C*H*C*H*OAc), 2.01 (3 H, s, MeCO), 1.70 (3 H, d, *J* 5.6, MeC=C) and 1.28 (3 H, d, *J* 6.0, *Me*CHOAc); *m/z* 128 (7%, M^+), 86 (75, M − CH_2CO) and 67 (100, C_5H_7) (Found: M^+, 128.0837. $C_7H_{12}O_2$ requires *M*, 128.0837).

(Z)-4-*Phenylbut*-3-*en*-2-*yl acetate* Z-**19a** (79%). R_f(hexane–Et_2O, 5:1) 0.5; ν_{max}(film)/cm^{-1} 1732 (C=O); $\delta(CDCl_3)$ 7.5–7.1 (5 H, m, Ph), 6.55 (1 H, d, *J* 12.5, PhC*H*=CH), 5.82 (1 H, dq, *J* 10.5 and 6.5, C*H*OAc), 5.65 (1 H, dd, *J* 12.5 and 10.5, PhCH=C*H*), 2.01 (3 H, s, MeCO) and 1.38 (3 H, d, *J* 6.5, *Me*CHOAc); *m/z* 190 (18%, M^+), 148 (87, M − CH_2CO), 131 (100, M − AcO) and 129 (70, M − AcOH − H) (Found: M^+, 190.0991. $C_{12}H_{14}O_2$ requires *M*, 190.0994).

(Z)-4-*Phenylbut*-3-*en*-2-*yl benzoate* (91%). Needles, m.p. 55–57 °C (from hexane); R_f(hexane–Et_2O, 20:1) 0.42; ν_{max}(CH_2Cl_2)/cm^{-1} 1710 (C=O); $\delta(CDCl_3)$ 8.1–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (8 H, m, *m*- and *p*-Hs Ph), 6.60 (1 H, d, *J* 11.1, PhC*H*=CH), 6.08 (1 H, dq, *J* 9.0 and 6.1, CHO), 5.79 (1 H, dd, *J* 11.1 and 9.0, PhCH=C*H*), and 1.51 (3 H, d, *J* 6.1, Me); *m/z* 252 (1%, M^+), 147 (31, M − PhCO) and 105 (100, PhCO) (Found: C, 80.9; H, 6.60. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.35%).

(Z)-5-*Methylhex*-3-*en*-2-*yl acetate* Z-**19b** (85%). R_f(light petroleum–Et_2O, 20:1) 0.25; ν_{max}(film)/cm^{-1} 1735 (C=O); $\delta(CDCl_3)$ 5.9–5.4 (1 H, m, C*H*OAc), 5.5–5.0 (2 H, m, CH=CH), 2.75 (1 H, m, C*H*Me_2), 2.00 (3 H, s, MeCO), 1.26 (3 H, d, *J* 6.3, *Me*CHOAc), 0.96 (3 H, d, *J* 6.6, CH*Me*$_A$*Me*$_B$) and 0.94 (3 H, d, *J* 6.6, CHMe_A*Me*$_B$); *m/z* 114 (8%, M − C_3H_6), 96 (35, M − AcOH) and 81 (100, M − AcOH − Me) (Found: M^+, 114.0682. $C_9H_{16}O_2$ requires *M* − C_3H_6, 114.0681).

(Z)-5-*Methylhex*-3-*en*-2-*yl benzoate* (94%). R_f(hexane–Et_2O, 20:1) 0.37; ν_{max}(film)/cm^{-1} 1718 (C=O); $\delta(CDCl_3)$ 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 5.92 (1 H, d quintet, *J* 1.4 and 6.3, C*H*OBz), 5.6–5.1 (2 H, m, CH=CH), 2.76 (1 H, d septet, *J* 2.0 and 6.6, C*H*Me_2), 1.41 (3 H, d, *J* 6.3, *Me*CHOBz), 0.99 (3 H, d, *J* 6.6, CH*Me*$_A$*Me*$_B$) and 0.98 (3 H, d, *J* 6.6, CHMe_A*Me*$_B$); *m/z* 218 (3%, M^+), 175 (2, M − C_6H_7), 105 (100, PhCO) and 77 (26, Ph) (Found: M^+, 218.1324. $C_{14}H_{18}O_2$ requires *M*, 218.1306).

(Z)-2-*Methylhex*-4-*en*-3-*yl acetate* Z-**20b** (84%). R_f(light petroleum–Et_2O, 20:1) 0.25; ν_{max}(film)/cm^{-1} 1735 (C=O); $\delta(CDCl_3)$ 5.71 (1 H, dq, *J* 10.5 and 6.7, CH=C*H*Me), 5.5–5.1 (2 H, m, CH=C*H*C*H*OAc), 2.3–1.5 (1 H, m, C*H*Me_2), 2.01 (3 H, s, MeCO), 1.70 (3 H, dd, *J* 6.7 and 1.2, CH=CHMe), 0.90 (3 H, d, *J* 6.7, CH*Me*$_A$Me$_B$) and 0.87 (3 H, d, *J* 6.7, CHMe_A*Me*$_B$); *m/z* 113 (11%, M − C_3H_7), 96 (35, M − AcOH) and 81 (100, M − AcOH − Me) (Found: M^+, 113.0603. $C_9H_{16}O_2$ requires *M* − C_3H_7, 113.0603).

(Z)-4-*Phenylbut*-3-*en*-2-*yl* N-*phenylcarbamate* Z-**29a** (99%). Needles, m.p. 57–58 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3411 (NH) and 1727 (C=O); $\delta(CDCl_3)$ 7.5–6.9 (10 H, m, 2 × Ph), 6.58 (1 H, s, NH), 6.56 (1 H, d, *J* 10.8, PhC*H*=CH), 5.87 (1 H, dq, *J* 8.8 and 6.2, CHO), 5.68 (1 H, dd, *J* 10.8 and 8.8, PhCH=C*H*) and 1.44 (3 H, d, *J* 6.2, Me); *m/z* 223 (3%, M − CO_2), 131 (100, M − $PhNHCO_2$), 93 (30, $PhNH_2$) and 91 (59, C_7H_7) (Found: C, 76.2; H, 6.60; N, 5.0. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.35; N, 5.2%).

(Z)-5-*Methylhex*-3-*en*-3-*yl* N-*phenylcarbamate* Z-**29b** (98%). R_f(hexane–Et_2O, 5:1) 0.35; ν_{max}(film)/cm^{-1} 3323 (NH) and 1700 (C=O); $\delta(CDCl_3)$ 7.5–6.9 (5 H, m, Ph), 6.56 (1 H, s, NH), 5.9–5.5 (1 H, m, CHO), 5.5–5.1 (2 H, m, CH=CH), 2.83 (1 H, m, C*H*Me_2), 1.35 (3 H, d, *J* 6.2, *Me*CHO), 1.00 (3 H, d, *J* 6.6, CH*Me*$_A$Me$_B$) and 0.97 (3 H, d, *J* 6.6, CHMe_A*Me*$_B$); *m/z* 233 (4%, M^+), 97 (24, M − $PhNHCO_2$), 93 (20, $PhNH_2$) and 55 (100, C_4H_7) (Found: M^+, 233.1403. $C_{14}H_{19}NO_2$ requires *M*, 233.1416).

(Z)-*Pent*-3-*en*-2-*yl* N-*phenylcarbamate* Z-**29c** (85% from *pent*-3-*yn*-2-*yl* N-*phenylcarbamate*).[32] Needles, m.p. 45–47 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3420 (NH) and 1721 (C=O); $\delta(CDCl_3)$ 7.5–6.9 (5 H, m, Ph), 6.58 (1 H, s, NH), 5.9–5.2 (3 H, m, CH=CHCHO), 1.74 (3 H, d, *J* 5.4, MeC=C) and 1.34 (3 H, d, *J* 6.1, *Me*CHO); *m/z* 205 (6%, M^+), 146 (18, M − CO_2NH), 93 (53, $PhNH_2$) and 69 (100, M − $PhNHCO_2$) (Found: C, 69.9; H, 7.4; N, 6.9. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.30; N, 6.8%).

(Z)-1-*Phenylbut*-2-*enyl* N-*phenylcarbamate* Z-**30a** (90%). R_f(hexane–Et_2O, 10:1) 0.26; ν_{max}(film)/cm^{-1} 3311 (NH) and 1710 (C=O); $\delta(CDCl_3)$ 7.6–6.9 (10 H, m, 2 × Ph), 6.70 (1 H, s, NH), 6.63 (1 H, d, *J* 7.7, PhC*H*), 6.0–5.5 (2 H, m, CH=CH) and 1.85 (3 H, d, *J* 5.2, Me); *m/z* 223 (6%, M − CO_2), 131 (100, M − $PhNHCO_2$), 93 (30, $PhNH_2$) and 91 (49, C_7H_7) (Found: M^+ − $PhNHCO_2$, 131.0862. $C_{17}H_{17}NO_2$ requires *M* − $PhNHCO_2$, 131.0860).

(Z)-2-*Methylhex*-4-*en*-3-*yl* N-*phenylcarbamate* Z-**30b** (76%). R_f(hexane–Et_2O, 5:1) 0.30; ν_{max}(film)/cm^{-1} 3323 (NH) and 1698 (C=O); $\delta(CDCl_3)$ 7.5–6.9 (5 H, m, Ph), 6.58 (1 H, s, NH), 5.73 (1 H, dq, *J* 10.2 and 6.7, CH=C*H*Me), 5.5–5.2 (2 H, m, CH=C*H*C*H*O), 1.88 (1 H, d septet, *J* 5.8 and 6.7, C*H*Me_2), 1.77 (3 H, dd, *J* 6.6 and 1.1, MeC=C), 0.97 (3 H, d, *J* 6.7, CH*Me*$_A$Me$_B$) and 0.93 (3 H, d, *J* 6.7, CHMe_A*Me*$_B$); *m/z* 233 (3%, M^+), 97 (57, M − $PhNHCO_2$), 93 (51, $PhNH_2$) and 55 (100, C_4H_7) (Found: M^+, 233.1423. $C_{14}H_{19}NO_2$ requires *M*, 233.1415).

(Z)-*But*-2-*enyl* N-*phenylcarbamate* Z-**35** (60%). Needles, m.p. 34–36 °C (from pentane); ν_{max}(CH_2Cl_2)/cm^{-1} 3448 (NH) and 1728 (C=O); $\delta(CDCl_3)$ 7.5–6.9 (5 H, m, Ph), 5.64 (1 H, s, NH), 6.0–5.3 (2 H, m, CH=CH), 4.74 (2 H, dq, *J* 5.6 and 0.8, CH_2O) and 1.73 (3 H, dt, *J* 5.2 and 0.8, MeC=C); *m/z* 191 (11%, M^+), 93 (52, $PhNH_2$) and 55 (100, M − $PhNHCO_2$) (Found: 69.0; H, 6.65; N, 7.4. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.80; N, 7.3%).

(Z)-4-*Trimethylsilylbut*-3-*en*-2-*yl* N-*phenylcarbamate* Z-**40a** (84%). Plates, m.p. 50–52 °C (from hexane); ν_{max}(CH_2Cl_2)/cm^{-1} 3407 (NH) and 1725 (C=O), $\delta(CDCl_3)$ 7.5–6.9 (5 H, m, Ph), 6.51 (1 H, s, NH), 6.27 (1 H, dd, *J* 14.2 and 8.2, C*H*=CHSi), 5.69 (1 H, d, *J* 14.2, CH=C*H*Si), 5.49 (1 H, dq, *J* 8.2 and 6.3, CHO), 1.35 (3 H, d, *J* 6.3, *Me*CHO) and 0.18 (9 H, s, $SiMe_3$); *m/z* 263 (18%, M^+), 127 (59, M − $PhNHCO_2$), 99 (100, CH=CHSiMe_3), 93 (71, $PhNH_2$) and 73 (90, $SiMe_3$) (Found: C, 63.8; 8.05; N, 5.3 $C_{14}H_{21}NO_{21}$ requires C, 63.9; H, 8.00; N, 5.3%).

(Z)-4-*Trimethylsilylbut*-3-*en*-2-*yl benzoate* Z-**40b** (95%). R_f(hexane–Et_2O, 20:1) 0.22; ν_{max}(film)/cm^{-1} 1730 (C=O); $\delta(CDCl_3)$ 8.2–7.9 (2 H, m, *o*-Hs Ph), 7.7–7.2 (3 H, m, *m*- and *p*-Hs Ph), 6.37 (1 H, dd, *J* 14.3 and 8.7, C*H*=CHSi), 5.72 (1 H, dq, *J* 8.7 and 6.3, C*H*OBz), 5.71 (1 H, d, *J* 14.3, CH=C*H*Si), 1.42 (3 H, d, *J*

6.3, MeCOBz) and 0.19 (9 H, s, $SiMe_3$); *m/z* 248 (1%, M^+), 143 (19, M − PhCO), 105 (100, PhCO), 77 (20, Ph) and 73 (72, $SiMe_3$) (Found: M^+, 248.1220. $C_{14}H_{20}O_2Si$ requires *M*, 248.1232).

(Z)-2-*Methyl*-4-*trimethylsilylbut*-3-*en*-2-*yl* N-*phenylcarbamate* **43** (81%). Needles, m.p. 36–38 °C (from pentane); ν_{max}(CH_2Cl_2)/cm^{-1} 3415 (NH) and 1725 (C=O); δ($CDCl_3$) 7.5–6.9 (5 H, m, Ph), 6.50 (1 H, s, NH), 6.43 (1 H, d, *J* 15.6, C*H*=CHSi), 5.53 (1 H, d, *J* 15.6, CH=C*H*Si), 1.64 (6 H, s, Me_2CO) and 0.20 (9 H, s, $SiMe_3$); *m/z* 277 (1%, M^+), 141 (25, M − $PhNHCO_2$), 93 (51, $PhNH_2$) and 73 (100, $SiMe_3$) (Found: C, 65.1; H, 8.5; N, 5.0. $C_{15}H_{17}NO_2Si$ requires C, 65.0; H, 8.30; N, 5.1%).

cis-(Z)-4-*Phenyl*-1-(*prop*-1-*enyl*)*cyclohexyl* N-*phenylcarbamate* **51** (90% *from the propargyl carbamate*).[29] A powder, m.p. 168–170 °C; R_f(hexane–Et_2OAc, 5:1) 0.23; ν_{max}(CH_2Cl_2)/cm^{-1} 3435 (NH) and 1728 (C=O); δ($CDCl_3$) 7.5–6.9 (10 H, m, 2 × Ph), 6.54 (1 H, s, NH), 5.89 (1 H, d, *J* 11.7, C*H*=CHMe), 5.68 (1 H, dq, *J* 11.7 and 5.6, CH=C*H*Me), 1.83 (3 H, d, *J* 5.6, CH=CH*Me*) and 2.9–1.4 (9 H, m, remainder); *m/z* 291 (1%, $M^+ - CO_2$), 199 (21, M − $PhNHCO_2$), 104 (42, PhNHC) and 93 (100, $PhNH_2$).

2-*Methyl*-4-*trimethylsilylbut*-3-*yn*-2-*ol*.—2-Methylbut-3-yn-2-ol (20.0 g, 0.238 mol) in dry ether (50 cm^3) was kept with ethylmagnesium bromide (0.595 mol) in ether (250 cm^3) under nitrogen at 0 °C for 20 h. Chlorotrimethylsilane (67.9 g, 0.625 mol) in dry ether (50 cm^3) was then added to it and the mixture refluxed for 2.5 h. The mixture was cooled to 0 °C, sulfuric acid (1.4 mol dm^{-3}; 100 cm^3) was added to it over 20 min and stirring continued for a further 10 min. The ether layer was then separated and the aqueous phase extracted with ether (2 × 50 cm^3). The combined extracts were washed with water (2 × 100 cm^3), aqueous sodium hydrogen carbonate (50 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was distilled to give the alcohol (25.6 g, 69%) as waxy needles, m.p. 38–39 °C (lit.,[70] 42 °C), b.p. 68–69 °C/13 mmHg (lit.,[70] 71 °C/18 mmHg; ν_{max}(CH_2Cl_2) 3568 (OH) and 2188 (C≡C); δ($CDCl_3$) 2.25 (1 H, s, OH), 1.50 (6 H, s, Me_2COH) and 0.12 (9 H, s, $SiMe_3$); *m/z* 141 (53%, M − Me), 123 (12, M − Me − H_2O) and 99 (100, M − C_3H_5O) (Found: M^+ − Me, 141.0735. $C_8H_{16}OSi$ requires *M* − Me, 141.0735).

4-*Trimethylsilylbut*-3-*yn*-2-*ol*. The same method described for the preparation of 2-methyl-4-trimethylsilylbut-3-yn-2-ol gave the alcohol[71] (8.04 g, 79%), b.p. 72 °C/13 mmHg; ν_{max}(film)/cm^{-1} 3010 (OH), 2200 (C≡C) and 1263 (SiMe); δ($CDCl_3$) 4.50 (1 H, q, *J* 6.6, C*H*OH), 1.87 (1 H, s, OH), 1.43 (3 H, d, *J* 6.6, *Me*CHOH) and 0.16 (9 H, s, $SiMe_3$); *m/z* 127 (10%, M − Me), 99 (100, M − C_2H_3O) and 84 (32, M − C_3H_6O) (Found: M^+ − Me, 127.0576. $C_7H_{14}OSi$ requires *M* − Me, 127.0579).

(E)-4-*Trimethylsilylbut*-3-*en*-2-*ol*. The same method described for the preparation of (*E*)-5-methylhex-3-en-2-ol, except that the reflux time was 1.5 h, gave the alcohol (2.17 g, 75%), b.p. 70–72 °C/14 mmHg (lit.,[72] 70 °C/30 mmHg); ν_{max}(film)/cm^{-1} 3330 (OH) and 1261 (SiMe); δ($CDCl_3$) 6.09 (1 H, dd, *J* 19.7 and 4.2, C*H*=CHSi), 5.74 (1 H, d, *J* 19.7, CH=C*H*Si), 4.23 (1 H, dq, *J* 4.2 and 6.4, C*H*OH), 1.91 (1 H, s, OH), 1.21 (3 H, d, *J* 6.4, *Me*CHOH) and 0.34 (9 H, s, $SiMe_3$).

Methylcuprate Reactions on the Acetates Z-**19a** *and* Z-**20a**.—Following Goering and Tseng,[73] methyllithium (1.4 mol dm^{-3} in Et_2O; 5.8 cm^3) was added to a stirred suspension of copper(I) iodide (0.77 g, 4.1 mmol) in dry ether (10 cm^3) under nitrogen at 0 °C. This mixture was stirred for 30 min after which the (*Z*)-acetate was added and stirring continued for a further 2 h. The reaction was quenched with aqueous ammonium chloride (15 cm^3) and extracted with ether (2 × 10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure and the residue was purified by preparative TLC (pentane) to give a similar mixture in each case of (*E*)-3-methyl-1-phenylbut-1-ene, (*E*)-4-phenylpent-2-ene and (*Z*)-3-methyl-1-phenylbut-1-ene (~0.25 g, 80%), identified by their known ^1H NMR spectra,[20] to those obtained by Goering from the *E*-isomers.

cis-5-*Methylcyclohex*-2-*enol*.—The enone (5.58 g) in dry ether (10 cm^3) was stirred with a suspension of lithium aluminium hydride (0.95 g) in dry ether (40 cm^3) under nitrogen at −78 °C for 1.5 h. The mixture was warmed to 0 °C and carefully quenched with aqueous ammonium chloride (30 cm^3). The resulting slurry was filtered through Celite and the Celite pad washed with ether (10 cm^3). The filtrate was separated, and the aqueous layer extracted with ether (2 × 10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the alcohol (3.85 g, 69%, as a 98:2 mixture with the *trans*-isomer), b.p. 78–80 °C/15 mmHg (lit.,[74] 95 °C/22 mmHg); δ($CDCl_3$) 5.74 (1 H, m, C*H*=CHCOH), 5.63 (1 H, dd, *J* 10.0 and 2.3, CH=C*H*COH), 4.35–4.25 (1 H, m, C*H*OH), 2.10–1.95 (2 H, m, equatorial Hs), 1.75–1.55 (2 H, m, MeC*H* and C=CCH_AH_B *cis* to Me), 1.62 (1 H, s, OH), 1.12 (1 H, td, *J* 11.9 and 10.1, CH_AH_BCOH *cis* to OH) and 0.96 (3 H, d, *J* 6.3, Me).

trans-5-*Methylcyclohex*-2-*enyl Benzoate* **45**.—Diethyl azodicarboxylate (1.305 g) in dry THF (15 cm^3) was added dropwise over 15 min to a stirred solution of the alcohol (0.560 g), triphenylphosphine (1.965 g) and benzoic acid (0.908 g) in dry THF (30 cm^3) under nitrogen at room temp. The mixture was stirred for 4 h, diluted with ether (60 cm^3), washed with aqueous sodium hydrogen carbonate (2 × 30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (hexane–Et_2O, 20:1) to give a 10:1 mixture of the *trans* benzoate and its *cis* isomer (0.820 g, 76%), HPLC (SiO_2, hexane–EtOAc, 99:1) gave the *benzoate*; R_f(hexane–Et_2O, 20:1) 0.4; ν_{max}(film)/cm^{-1} 1709 (C=O); δ($CDCl_3$) 8.1–8.0 (2 H, m, *o*-Hs Ph), 7.6–7.2 (3 H, m, *m*- and *p*-Hs Ph), 6.04 (1 H, ddd, *J* 9.9, 5.0 and 2.0, C*H*=CHCOBz), 6.0–5.8 (1 H, m, CH=C*H*COBz), 5.50 (1 H, m, C*H*OBz), 2.22 (1 H, dt, *J* 17.9 and 5.0, C=CCH_AH_B *trans* to Me), 2.1–1.9 (2 H, m, MeC*H* and CH_AH_B COBz *cis* to OBz), 1.66 (1 H, ddd, *J* 17.9, 10.1 and 2.0, C=CCH_AH_B *cis* to Me), 1.52 (1 H, ddd, *J* 14.5, 12.5 and 4.2, CH_AH_BCOBz *trans* to OBz) and 1.01 (3 H, d, *J* 6.5, Me); *m/z* 216 (7%, M^+), 160 (7, M − C_4H_8) and 105 (100, PhCO) (Found: M^+, 216.1151. $C_{14}H_{16}O_2$ requires *M*, 216.1150).

trans-5-*Methylcyclohex*-2-*enyl* N-*Phenylcarbamate* **49**.—The benzoate **45** (0.75 g, 10:1 mixture with **48**) in dry ether was stirred with a suspension of lithium aluminium hydride (0.07 g) in ether (10 cm^3) under nitrogen at 0 °C for 4 h and the mixture worked up in the usual way. The resulting mixture of alcohols (0.71 g) was added to triethylamine (0.70 g), acetic anhydride (0.35 g) and DMAP (0.02 g) in dry dichloromethane (10 cm^3), and kept for 3 h in order to esterify the benzyl alcohol. Phenyl isocyanate (0.42 g) was then added to the mixture which was kept for 10 h. The mixture was washed with aqueous sodium hydrogen carbonate (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (hexane–Et_2O, 10:1) and further purified by HPLC (SiO_2, hexane–EtOAc, 20:1) to give the carbamate (0.185 g, 38%) as needles, m.p. 95–96 °C (from hexane) (lit.,[26] 99–100 °C); ν_{max}(CH_2Cl_2)/cm^{-1} 3399 (NH) and 1723 (C=O); δ($CDCl_3$) 7.4–7.0 (5 H, m, Ph), 6.56 (1 H, s, NH), 6.03 (1 H, ddd, *J* 9.9, 5.0 and 2.2, C*H*=CHCO), 5.9–5.8 (1 H, m, CH=C*H*CO), 5.4–5.2 (1 H, m, CHO), 2.19 (1 H, dt, *J* 17.8 and 5.0, C=CCH_BH_B *trans* to Me), 2.0–1.8 (2 H, m, C*H*Me and CH_AH_BCOR *cis* to OR), 1.59 (1 H, dddd, *J* 17.8, 10.3, 4.2 and 2.2, C=CCH_AH_B *cis* to Me), 1.47 (1 H, ddd, *J* 14.6, 12.7 and 4.3, CH_AH_BCOR *trans* to OR) and 0.99

(3 H, d, *J* 6.5, Me); *m/z* 231 (3%, M^+), 187 (5, M − CO_2), 95 (100, M − $PhNHCO_2$) and 93 (92, $PhNH_2$) (Found: C, 72.9; H, 7.40; N, 6.1. $C_{14}H_{17}NO_2$ requires C, 72.7; H, 7.35; N, 6.1%).

Dimethyl(phenyl)-1-(1-phenylbutyl)silane.—Palladium (10% on C) in methanol (5 cm^3) was stirred under hydrogen at 1 atm for 30 min. The allylsilane *E*-**21a** (0.484 g) in methanol (10 cm^3) was added to the mixture which was then stirred under hydrogen at 1 atm for 2 h. The catalyst was filtered off and the filtrate evaporated under reduced pressure. The residue was chromatographed (hexane) to give the *silane* (0.361 g, 74%); R_f(hexane) 0.25; ν_{max}(film)/cm^{-1} 1603 (Ph), 1261 (SiMe) and 1128 (SiPh); δ($CDCl_3$) 7.5–6.8 (10 H, m, 2 × Ph), 2.62 (1 H, dd, *J* 9.6 and 5.4, PhC*H*), 2.9–0.5 (7 H, m, Pr), 0.24 (3 H, s, $SiMe_AMe_B$) and 0.16 (3 H, s, $SiMe_A\mathit{Me}_B$); *m/z* 268 (11%, M^+) and 135 (100, $PhMe_2Si$) (Found: M^+, 268. 1643. $C_{18}H_{24}Si$ requires *M*, 268. 1647).

(±)-1-*Phenylbutanol.*—Boron trifluoride (40% solution in acetic acid; 0.05 cm^3) was stirred with the silane (100 mg) in dry dichloromethane (2 cm^3) at 20 °C under nitrogen for 1.5 h. Aqueous sodium hydrogen carbonate (3 cm^3) was added cautiously to the mixture and stirring continued for 15 min. The mixture was diluted with ether (15 cm^3) after which the aqueous layer was separated and extracted with ether (5 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give fluoro(dimethyl)-1-(1-phenylbutyl)-silane (75 mg, 96%); δ($CDCl_3$) 7.5–7.0 (5 H, m, Ph), 2.4–1.1 (5 H, m, $SiCHCH_2CH_2$), 0.84 (3 H, t, *J* 6 Hz, Me) and 0.12 (6 H, d, *J* 7, $SiMe_2$). This fluorosilane (75 mg) was stirred in dry ether (2 cm^3) with triethylamine (40 mg) and *m*-chloroperbenzoic acid (300 mg) at room temp. for 20 h. The mixture was diluted with ether (20 cm^3) and then washed with aqueous sodium bisulfite (10 cm^3) and aqueous sodium hydrogen carbonate (10 cm^3); the combined aqueous washings were then extracted with ether (10 cm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC (CH_2Cl_2) to give the alcohol (41 mg, 74%), b.p. 120 °C/19 mmHg (lit.,[63] 113–115 °C/17 mmHg); ν_{max}(film) 3340 (OH) and 1604 (Ph); δ($CDCl_3$) 7.5–7.2 (5 H, m, Ph), 4.67 (1 H, t, *J* 5, PhC*H*), 1.89 (1 H, s, OH) and 2.0–0.7 (7 H, m, remainder); identical with a sample (4.98 g, 78%) prepared from benzaldehyde (4.50 g) and propylmagnesium bromide (50 mmol) in dry ether (60 cm^3) under nitrogen at 0 °C for 3 h.

(R)-4-*Phenylbut-3-yn-2-ol* **56**.—Alpine-borane® (0.5 mol dm^{-3} in THF, Aldrich; 46 cm^3) was stirred under nitrogen at water pump pressure and then under high vacuum until all solvent was removed. The nitrogen atmosphere was then restored and and the mixture cooled to 0 °C, when 4-phenylbut-3-yn-2-one[75] (2.4 g) in dry pentane (5 cm^3) was added to it; the mixture was then stirred at 0 °C for 8 h and then at room temp. for 10 h. The mixture was re-cooled to 0 °C and, after addition of acetaldehyde (1 cm^3), was stirred for 15 min. The solvent was removed at water pump pressure, and the pinene was removed at high vacuum at 40 °C for 2 h. The nitrogen atmosphere was restored and dry ether (40 cm^3) was added to the solution which was then cooled to 0 °C. After addition of 2-aminoethanol (1.5 cm^3) to the solution stirring was continued at 0 °C for 20 min. The resulting slurry was filtered through Celite and the pad washed with ether (10 cm^3). The filtrate was washed with brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (hexane–Et_2O, 5:1) to give the (*R*)-alcohol (1.97 g, 81%); R_f(hexane–Et_2O, 5:1) 0.2 $[\alpha]_D^{20}$ +25.4* (*c* 0.30, $CHCl_3$), identical (^1H NMR, IR) with the racemic alcohol. The following homochiral derivatives were prepared from this compound by the same methods as described for the preparation of the corresponding racemic compounds.

(R)-4-*Phenylbut-3-yn-2-yl benzoate.* $[\alpha]_D^{20}$ +16.6 (*c* 0.85, $CHCl_3$).

(R)-4-*Phenylbut-3-yn-2-yl* N-*phenylcarbamate.* M.p. 85–86 °C (from hexane), $[\alpha]_D^{20}$ +148 (*c* 0.24, $CHCl_3$).

(Z,R)-4-*Phenylbut-3-en-2-yl benzoate* **57**. $[\alpha]_D^{20}$ −171 (*c* 0.83, $CHCl_3$).

(Z,R)-4-*Phenylbut-3-en-2-yl* N-*phenylcarbamate* **53**. From unrecrystallised propargyl carbamate, $[\alpha]_D^{20}$ −131 (*c* 0.35, $CHCl_3$).

(E,S)-1-*Dimethyl(phenyl)silyl-1-phenylbut-2-ene* **54**. $[\alpha]_D^{20}$ +4.25 (*c* 0.55, $CHCl_3$).

(R)-*Dimethylphenyl-1-(1-phenylbutyl)silane.* From the mixture of **58** and **59**, $[\alpha]_D^{20}$ +11.6 (*c* 0.63, $CHCl_3$).

(S)-*Dimethylphenyl-1-(1-phenylbutyl)silane.* From **54**, $[\alpha]_D^{20}$ −16.1 (*c* 0.65, $CHCl_3$).

(R)-1-*Phenylbutan-1-ol* **60**. From the mixture of **58** and **59**, $[\alpha]_D^{20}$ +22.2 (*c* 0.30, $CHCl_3$).

(S)-1-*Phenylbutan-1-ol* **55**. From **54**, $[\alpha]_D^{20}$ −33.6 (*c* 0.38, $CHCl_3$).

α-*Methoxy-α-(trifluoromethyl)phenylacetate Ester Formation.*—The alcohol (0.02 mmol), DMAP (0.01 mmol), Mosher's acid (0.03 mmol) and dicyclohexylcarbodiimide (0.03 mmol) were kept in dichloromethane (0.3 cm^3) under nitrogen for 25 h. The mixture was purified directly by preparative TLC (CH_2Cl_2–hexane, 1:1) to give the esters (80–90%). The following MTPA esters were prepared in this way and characterised by their ^1H NMR spectra.

(R)-4-*Phenylbut-3-yn-2-yl* (R)-*methoxy(trifluoromethyl)-phenylacetate.* δ($CDCl_3$) 7.6–7.2 (10 H, m, 2 × Ph), 5.90 (1 H, q, *J* 6.7, CHO), 3.61 (3 H, q, *J* 0.9, OMe) and 1.61 (3 H, d, *J* 6.7, MeCH).

(S)-4-*Phenylbut-3-yn-2-yl* (R)-*methoxy(trifluoromethyl)-phenylacetate.* δ($CDCl_3$) 7.6–7.2 (10 H, m, 2 × Ph), 5.86 (1 H, q, *J* 6.8, CHO), 3.58 (3 H, q, *J* 1.1, OMe) and 1.66 (3 H, d, *J* 6.8, MeCH).

(S)-1-*Phenylbutyl* (S)-*methoxy(trifluoromethyl)phenylacetate.* δ($CDCl_3$) 7.5–7.2 (10 H, m, 2 × Ph), 5.96 (1 H, dd, *J* 8.1 and 5.9, PhC*H*), 3.43 (3 H, q, *J* 1.1, OMe), 2.1–1.1 (4 H, m, CH_2CH_2) and 0.86 (3 H, t, *J* 7.3, Me).

(R)-1-*Phenylbutyl* (S)-*methoxy(trifluoromethyl)phenylacetate.* δ($CDCl_3$) 7.5–7.2 (10 H, m, 2 × Ph), 5.88 (1 H, dd, *J* 8.0 and 6.1, PhC*H*), 3.53 (3 H, q, *J* 1.2, OMe), 2.1–1.1 (4 H, m, CH_2CH_2) and 0.92 (3 H, t, *J* 7.3, Me).

Note: The enantiomer of Mosher's acid was used for the derivatives of the 'saturated' alcohols from that which was used for the acetylenic alcohols.

The ^1H NMR spectra showed that the alcohol **56** had a 78% e.e., the alcohol **60** had a 52% e.e. and the alcohol **55** had a 72% e.e.

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References

1 I. Fleming, J. Dunoguès and R. Smithers, *Org. React.* (*N.Y.*), 1989, **37**, 57.
2 H. Wetter and P. Scherer, *Helv. Chim. Acta*, 1983, **66**, 118.
3 V. G. Matassa, P. R. Jenkins, A. Kümin, L. Damm, J. Schreiber, D. Felix, E. Zass and A. Eschenmoser, *Isr. J. Chem.*, 1989, **29**, 321.

* $[\alpha]_D$ Values are recorded in units of 10^{-1} deg cm^2 g^{-1}.

4 T. Hayashi, M. Konishi, H. Ito and M. Kumada, *J. Am. Chem. Soc.*, 1982, **104**, 4962; T. Hayashi, M. Konishi and M. Kumada, *J. Am. Chem. Soc.*, 1982, **104**, 4963; T. Hayashi, H. Ito and M. Kumada, *Tetrahedron Lett.*, 1982, **23**, 4605; T. Hayashi, M. Konishi and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1983, 736; T. Hayashi, K. Kabeta, T. Yamamoto, K. Tamao and M. Kumada, *Tetrahedron Lett.*, 1983, **24**, 5661; T. Hayashi, Y. Okamoto, K. Kabeta, T. Hagihara and M. Kumada, *J. Org. Chem.*, 1984, **49**, 4224; T. Hayashi, M. Konishi, Y. Okamoto, K. Kabeta and M. Kumada, *J. Org. Chem.*, 1986, **51**, 3772; T. Hayashi, Y. Matsumoto and Y. Ito, *Organometallics*, 1987, **6**, 884.

5 G. Wickham and W. Kitching, *Organometallics*, 1983, **2**, 541; G. Wickham, D. Young and W. Kitching, *Organometallics*, 1988, **7**, 1187; W. Kitching, K. G. Penman, B. Laycock and I. Maynard, *Tetrahedron*, 1988, **44**, 3819.

6 I. Fleming and N. K. Terrett, *J. Organomet. Chem.*, 1984, **264**, 99; M. J. C. Buckle, I. Fleming and S. Gil, *Tetrahedron Lett.*, 1992, **33**, 4479.

7 Preliminary communication: I. Fleming, A. K. Sarkar and A. P. Thomas, *J. Chem. Soc., Chem. Commun.*, 1987, 157; full paper: I. Fleming, N. J. Lawrence, A. K. Sarkar and A. P. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3303.

8 Preliminary communication: I. Fleming and N. J. Lawrence, *Tetrahedron Lett.*, 1988, **29**, 2073 and 2077; full paper: I. Fleming and N. J. Lawrence, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3309.

9 Preliminary communication: I. Fleming and D. Higgins, *J. Chem. Soc., Perkin Trans. 1*, 1989, 206; full paper: I. Fleming and D. Higgins, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3327.

10 T. K. Sarkar, *Synthesis*, 1990, 969 and 1101.

11 Preliminary communication: I. Fleming and A. K. Sarkar, *J. Chem. Soc., Chem. Commun.*, 1986, 1199; full paper: I. Fleming, S. Gil, A. K. Sarkar and T. Schmidlin, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3351.

12 I. Fleming and A. P. Thomas, *J. Chem. Soc., Chem. Commun.*, 1985, 411 and 1986, 1456.

13 I. Fleming and D. Marchi, *Synthesis*, 1981, 560.

14 B. Laycock, W. Kitching and G. Wickham, *Tetrahedron Lett.*, 1983, **24**, 5785; see also B. M. Trost and D. M. T. Chan, *J. Chem. Soc.*, 1982, **104**, 3733.

15 H.-F. Chow and I. Fleming, *Tetrahedron Lett.*, 1985, **26**, 397; I. Fleming, P. E. J. Sanderson and N. K. Terrett, *Synthesis*, 1992, 69.

16 I. Fleming, D. Marchi and S. K. Patel, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2518.

17 B. M. Trost, J. Yoshida and M. Lautens, *J. Am. Chem. Soc.*, 1983, **105**, 4494; see also Y. Okuda, M. Sato, K. Oshima and H. Nozaki, *Tetrahedron Lett.*, 1983, **24**, 2015; S. Torii, H. Tanaka, T. Katoh and K. Morisaki, *Tetrahedron Lett.*, 1984, **25**, 3207; H. Urata, H. Suzuki, Y. Moro-Oka and T. Ikawa, *Bull. Chem. Soc. Jpn.*, 1984, **57**, 607.

18 J. G. Smith, S. E. Drozda, S. P. Petraglia, N. R. Quinn, E. M. Rice, B. S. Taylor and M. Viswanathan, *J. Org. Chem.*, 1984, **49**, 4112.

19 R. J. Anderson, C. A. Henrick and J. B. Siddall, *J. Am. Chem. Soc.*, 1970, **92**, 735; R. M. Magid, *Tetrahedron*, 1980, **36**, 1901.

20 H. L. Goering, E. P. Seitz and C. C. Tseng, *J. Org. Chem.*, 1981, **46**, 5304.

21 R. J. Anderson, C. A. Henrick, J. B. Siddall and R. Zurflüh, *J. Am. Chem. Soc.*, 1972, **94**, 5379; see also ref. 17.

22 H. L. Goering and S. S. Kantner, *J. Org. Chem.*, 1983, **48**, 721; M. Julia, A. Righini and J.-N. Verpeaux, *Tetrahedron Lett.*, 1979, 2393; A. Claesson and L.-I. Olsson, *J. Chem. Soc., Chem. Commun.*, 1978, 621; see also E. J. Corey and N. W. Boaz, *Tetrahedron Lett.*, 1984, **25**, 3063.

23 I. Fleming and T. W. Newton, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1805; A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Res.*, 1990, (S), 291; A. Barbero, P. Cuadrado, I. Fleming, A. M. González and F. J. Pulido, *J. Chem. Soc., Chem. Commun.*, 1992, 351.

24 A. Miyashita and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1102; A. Miyashita, T. Yamamoto and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1109; M. Suzuki, T. Suzuki, T. Kawagishi and R. Noyori, *Tetrahedron Lett.*, 1980, **21**, 1247.

25 C. Gallina and P. G. Ciattini, *J. Am. Chem. Soc.*, 1979, **101**, 1035.

26 H. L. Goering, S. S. Kantner and C. C. Tseng, *J. Org. Chem.*, 1983, **48**, 715.

27 I. Fleming and D. Waterson, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1809.

28 Y. Tanigawa, Y. Fuse and S.-I. Murahashi, *Tetrahedron Lett.*, 1982, **23**, 557.

29 I. Fleming, K. Takaki and A. P. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2269.

30 J. Levisalles, M. Rudler-Chauvin and H. Rudler, *J. Organomet. Chem.*, 1977, **136**, 103.

31 M. M. Midland, A. Tramontano, A. Kazubski, R. S. Graham, D. J. S. Tsai and D. B. Cardin, *Tetrahedron*, 1984, **40**, 1371.

32 H. C. Brown, G. G. Pai and P. K. Jadhav, *J. Am. Chem. Soc.*, 1984, **106**, 1531.

33 I. Fleming, R. Henning and H. Plaut, *J. Chem. Soc., Chem. Commun.*, 1984, 29.

34 R. MacLeod, F. J. Welch and H. S. Mosher, *J. Am. Chem. Soc.*, 1960, **82**, 876; H. M. Peters, D. M. Feigl and H. S. Mosher, *J. Org. Chem.*, 1968, **33**, 4245.

35 J. A. Dale, D. L. Dull and H. S. Mosher, *J. Org. Chem.*, 1969, **34**, 2543.

36 H.-F. Chow and I. Fleming, *Tetrahedron Lett.*, 1985, **26**, 397.

37 G. Höfle and W. Steglich, *Synthesis*, 1972, 619; G. Höfle, W. Steglich and H. Vorbrüggen, *Angew. Chem., Internat. Ed. Engl.*, 1978, **17**, 569.

38 C. U. Pitman, Jr. and G. A. Olah, *J. Am. Chem. Soc.*, 1965, **87**, 5632.

39 A. L. Gemal and J.-L. Luche, *J. Am. Chem. Soc.*, 1981, **103**, 5454.

40 G. H. Posner and C. M. Lentz, *J. Am. Chem. Soc.*, 1979, **101**, 934.

41 I. Paterson, *Tetrahedron*, 1988, **44**, 4207.

42 W. C. Agosta and A. B. Smith III, *J. Am. Chem. Soc.*, 1971, **93**, 5513.

43 J. T. A. Reuvers and A. De Groot, *Synthesis*, 1982, 1105.

44 A. Hassner and T. C. Mead, *Tetrahedron*, 1964, **20**, 2201.

45 H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, 1951, **73**, 5863 and 1954, **76**, 5405.

46 O. Mitsunobu, *Synthesis*, 1981, 1.

47 I. Fleming, T. W. Newton and F. Roessler, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2527.

48 J. Slutzky and H. Kwart, *J. Am. Chem. Soc.*, 1973, **95**, 8678.

49 K. Fugami, K. Oshima, K. Utimoto and H. Nozaki, *Tetrahedron Lett.*, 1986, **27**, 2161.

50 I. Fleming, M. Rowley, P. Cuadrado, A. M. González-Nogal and F. J. Pulido, *Tetrahedron*, 1989, **45**, 413.

51 M. S. Wrighton and M. A. Schroeder, *J. Am. Chem. Soc.*, 1974, **96**, 6235.

52 R. A. Benkeser, M. L. Burrows, L. E. Nelson and J. V. Swisher, *J. Am. Chem. Soc.*, 1961, **83**, 4385.

53 J. V. Swisher and C. Zullig, Jr., *J. Org. Chem.*, 1973, **38**, 3353.

54 G. A. Hiegel and P. Burk, *J. Org. Chem.*, 1973, **38**, 3637.

55 M. E. Krafft and R. A. Holton, *Tetrahedron Lett.*, 1983, **24**, 1345.

56 Y. Chan and W. W. Epstein, *Org. Synth.*, Coll. Vol. VI, 1988, 496.

57 R. F. Miller and R. Adams, *J. Am. Chem. Soc.*, 1936, **58**, 787.

58 J. Colonge and J. Grenet, *Bull. Soc. Chim. Fr.*, 1954, 1304.

59 E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1951, 2078 and 2085.

60 J. Kenyon, S. M. Partridge and H. Phillips, *J. Chem. Soc.*, 1937, 207.

61 J. Kenyon, S. M. Partridge and H. Phillips, *J. Chem. Soc.*, 1936, 85.

62 R. G. R. Bacon and E. H. Farmer, *J. Chem. Soc.*, 1937, 1065.

63 C. R. Weast, ed., Handbook of Chemistry and Physics, CRC, Florida, 62nd Edition, 1981.

64 S. A. Morell, H. H. Geller and E. C. Lathrop, *Ind. Eng. Chem. Fundam.*, 1945, **37**, 877.

65 W. S. Linn, W. L. Waters and M. C. Caserio, *J. Am. Chem. Soc.*, 1970, **92**, 4018.

66 K. Alder and F. H. Flock, *Chem. Ber.*, 1956, **89**, 1732.

67 K. Jankowski and J.-Y. Daigle, *Can. J. Chem.*, 1971, **49**, 2594.

68 M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, 1960, 3563.

69 J. Reif, *Ber.*, 1908, **41**, 2739.

70 M. F. Shostakovski, I. E. Shikhiev and N. V. Komarov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, 1956, 1271 (*Chem. Abstr.*, 1961, **51**, 5689i).

71 G. E. Bennett and W. W. Lee, U.S. Patent 2887371 (1959) (*Chem. Abstr.*, 1959, **53**, 19883e).

72 J.-P. Picard. A. Ekouya, J. Dunoguès, N. Duffaut and R. Calas, *J. Organomet. Chem.*, 1972, **93**, 51.

73 H. L. Goering and C. C. Tseng, *J. Org. Chem.*, 1983, **48**, 3986.

74 H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, 1954, **76**, 5405.

75 L. Birkofer, A. Ritter and H. Uhlenbrauck, *Chem. Ber.*, 1963, **96**, 3280.

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