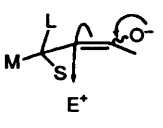
The Diastereoselectivity of Electrophilic Attack on Trigonal Carbon Adjacent to a Stereogenic Centre: Diastereoselective Protonation, Epoxidation and Acylation of Allylsilanes

Ian Fleming * **and Jeremy J. Lewis**
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

The four allylsilanes **6** and **8**, which have a stereogenic centre carrying a phenyl group, a methyl group and a hydrogen atom adjacent to the nucleophilic end of the double bond, react with protic (or deuteronic) acid, *m*-chloroperbenzoic acid and chlorosulfonyl isocyanate to give electrophilic substitution of the allylsilane, with diastereoselectivity in the sense **2**, in conformity to a general rule for electrophilic attack on a double bond adjacent to a stereogenic centre. The most reliably stereoselective reactions took place with the allylsilane **6b**, in which the stereogenic centre is *cis* to a group larger than a hydrogen atom in both the *E*- and *Z*-isomer. In general, chlorosulfonyl isocyanate induces higher stereoselectivity than the peracid, and the peracid higher stereoselectivity than the proton (or deuteron).

In the preceding paper,[1] we described the diastereoselectivity of attack by two electrophiles, methyl iodide and a proton, on enolates **1** that have an adjacent sterogenic centre. We have continued our investigation by changing the nucleophile from an enolate double bond to the less powerfully nucleophilic double bond of an allylsilane, for which the analogous transition structure **2** should be very similar. Necessarily, we



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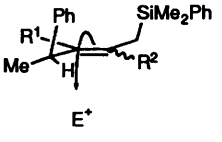

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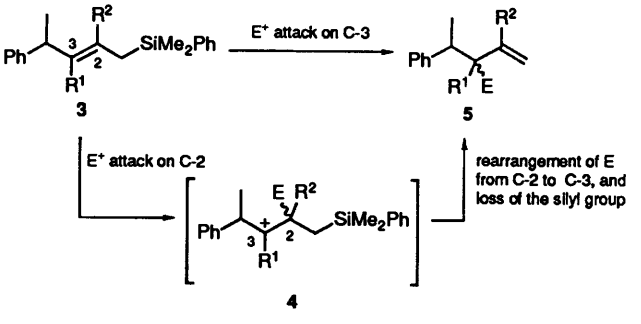
have also changed the electrophile to something more powerful, since methyl iodide does not react with allylsilanes. We chose three electrophiles of deliberately different types—the proton, as in the preceding paper, a heteroatom electrophile in the form of *m*-chloroperbenzoic acid (MCPBA) and a carbon electrophile, chlorosulfonyl isocyanate (CSI). For this work, we restricted ourselves to a stereogenic centre having a phenyl group as the large group, a methyl group as the medium-sized group and a hydrogen atom as the small group, but we investigated all four possible kinds of allylsilane, one with a disubstituted double bond ($R^1 = R^2 = H$), the two with a trisubstituted double bond ($R^1 = Me$, $R^2 = H$ and $R^1 = H$, $R^2 = Me$), and one with a tetrasubstituted double bond ($R^1 = R^2 = Me$). We hoped to fond out whether the degree of diastereoselectivity in favour of electrophilic attack taking place in the sense of the arrow in the enolate **1** would hold up when the balance of nucleophilicity and electrophilicity changed to the allylsilane **2**. We had, of course, every expectation, following the arguments advanced in the preceding paper, that the major diastereoisomer would continue to be that produced in the same stereochemical sense, and we were reasonably confident, from our own earlier work and that of many others,[2] that the regiochemistry of attack on the allylsilanes would also take place largely in the sense of **2**, at least when R^1 was a hydrogen atom. In addition, we hoped to learn something of how well behaved the different allylsilanes were when they carried substituents in these four different arrangements, for we already had reason to believe that there were likely to be problems when R^1 was a methyl group.[3] The results reported in this paper have not been published in preliminary form, although they have appeared in the tables of a chapter in *Organic Reactions*.[2] Some related results in agreement with ours, but with only two close counterparts, have recently been published by Taddei and his co-workers.[4]

It is convenient to deal with the four allylsilanes in two categories, those with a hydrogen atom at C-3 ($R^1 = H$ in **3**) and those with a methyl group at C-3 ($R^1 = Me$ in **3**). The reason is that these can be expected to behave with different degrees of regioselectivity, with the former reacting in a well-behaved manner, the electrophile attacking directly at C-3, and losing the silyl group shortly thereafter, **3**→**5**. Allylsilanes **3**,

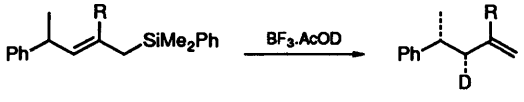


with $R^1 = Me$, may well suffer substantial attack by the electrophile at C-2, giving an intermediate **4**, as well as directly at C-3, with the final product **5** of electrophilic substitution following only after a migration of the electrophilic group E from C-2 to C-3.[3] This rearrangement can take place after rotation about the C-2–C-3 bond in the intermediate cation **4**, and the stereochemistry of the initial attack may, therefore, be lost in the final product. The alternative rearrangement, of the R^2 group from C-2 to C-3, is at most a minor pathway. When E is a hydrogen atom and R^2 is methyl, hydride migration takes place, as in **4** → **5**,[5] rather than methyl migration, and when E is an electrophilic group like acyl, the migration of R^2 to leave a cation adjacent to E is unlikely.

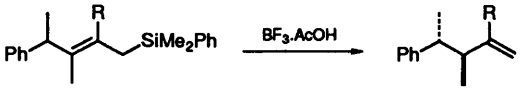
Results and Discussion

Diastereoselective Attack by Electrophiles.—The allylsilanes **6a** and **6b** reacted with the boron trifluoride–deuteroacetic acid complex to give the alkenes **7**, where we draw only what we expect to be the major diastereoisomers. We measured the ratio

of diastereoisomers directly by ^{1}H NMR spectroscopy, using the moderately well-resolved signals from the diastereotopic protons at the newly created stereogenic centre. However, we cannot claim with certainty that the sense of the selectivity is that shown in the structures **7a** and **7b**. The allylsilanes **8a** and **8b** similarly underwent clean protodesilylation to give the alkenes **9**. The diastereoselectivity was not impressive in either case, perhaps for the reasons discussed above, but we were easily able to prove that the stereochemistry of the major product **9b** was that shown (see below). Accordingly, we have little doubt that **7b** and **9a** are also the major products, but the stereochemistry of the alkene **7a** is very uncertain, because the stereogenic centre is *cis* to a hydrogen atom in the major stereoisomer of the allylsilane **6a**, and this has consequences (see below).



6a R = H	*E*:*Z* 89:11		**7a**	71%	52:48
6b R = Me	*E*:*Z* 74:26		**7b**	92%	80:20



8a R = H	*E*:*Z* 64:36		**9a**	75%	56:44
8b R = Me	*E*:*Z* 74:26		**9b**	86%	60:40

The allylsilane **8b** resembles in its substitution pattern the enolate, numbered **10a** in the preceding paper. The diastereoselectivity of its protonation is rather less than that of the enolate (60:40 compared to 85:15), but the ambiguity about where the proton initially attacks the allylsilane removes any force from this observation, and the reactions were, in any case, carried out at very different temperatures, 0 °C for the allylsilanes and −78 °C for the enolates. The diastereoselectivity in favour of the formation of the alkene **7b** is noticeably greater than that for any of the others. This is understandable, first because in this allylsilane there is no ambiguity about where the deuteron initially attacks, and secondly there is little doubt that its conformation in the ground state is close to that illustrated in **2**. On the other hand, the allylsilane **7a** is predominantly *E* (89:11), and the substituent *cis* to the stereogenic centre on the double bond is only a hydrogen atom. The degree of A ^{1,3} strain is attenuated, and an alternative conformation, in which the methyl group eclipses or partially eclipses the double bond, is likely to be substantially populated. Molecules in this conformation can be expected to react with opposite diastereoselectivity in electrophilic attack, and the overall diastereoselectivity (52:48) is therefore unimpressive, and, for that matter, uncertain in its sense. It is especially unimpressive considering that the minor (11%) *Z* isomer of the allylsilane has, in all probability, reacted with relatively high diastereoselectivity in the sense favouring the formation of the isomer **7a**. It seems likely that the *E* isomer has actually undergone deuteriodesilylation to give mainly the isomer not illustrated. The same problem arises with the allylsilane **8a**, where the starting material is not as rich in the *E* isomer (64:36), and the ratio we observe (56:44) is very likely to be a composite of two very different numbers. We[6] and others,[7] with several different substrates, have elsewhere found significantly lower levels of diastereoselectivity when the substituent on the double bond *cis* to an allylic stereogenic centre is only a hydrogen atom. This problem did not arise in the enolate work described in the preceding paper, because all of the enolates had an alkyl, aryl, alkoxy or oxyanion group in that position. We find, in general, that only the allylsilane **6b** consistently shows high diastereoselectivity, remarkably so considering that only the difference between a phenyl and a methyl group differentiate the two faces of the double bond. With this compound, and also with the allylsilane **8b**, the geometry of the double bond is probably not important.

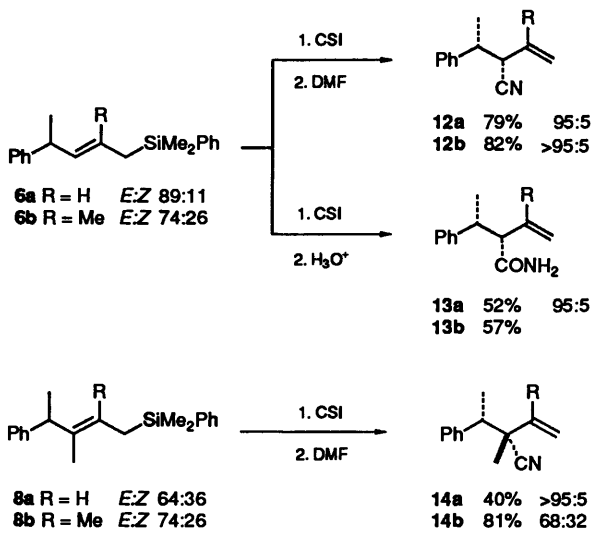
Epoxidation of all four allylsilanes with MCPBA led to unstable epoxides, which we treated immediately with tetrabutylammonium fluoride to convert them into the allylic alcohols **10** and **11**. In this series of experiments, we know the

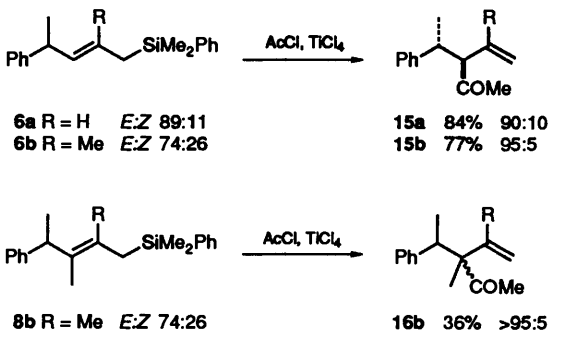
6a R = H	*E*:*Z* 89:11		**10a**	71%	57:43
6b R = Me	*E*:*Z* 74:26		**10b**	85%	92:8

8a R = H	*E*:*Z* 64:36		**11a**	76%	57:43
8b R = Me	*E*:*Z* 74:26		**11b**	81%	73:27

relative configurations of the pairs of products in all four cases (see below). The major product is in each case that expected from the model **2**. There is no problem this time with the electrophile's attacking at C-2—this is a bridging electrophile that attacks simultaneously at both C-2 and C-3. The ratios of diastereoisomers is, therefore, a direct and reliable measure of the diastereoselectivity of attack on the double bonds. The results are in close agreement with those described above for deuterodesilylation and prodesilylation, indicating perhaps that our caution in establishing that some of those results might not be too reliable, is unwarranted. The result with the allylsilane **6a** is similar to that obtained by Taddei (62%; 55:45)[4] using an allylsilane having a trimethylsilyl group in place of the phenyldimethylsilyl group. As before, the results for the allylsilanes **6a** and **8a** are probably composites of two different numbers, one for the *E*-isomer and one for the *Z*. The only result of much significance is again the high level of diastereoselectivity (92:8) in the epoxidation of the allylsilane **6b**, with **8b** giving a ratio (73:27) not much lower. The presence of a substituent on C-2 is clearly helpful.

Our third electrophile, CSI, reacted as we had expected from earlier work establishing this powerful and well-behaved carbon electrophile for use with allylsilanes.[8] We treated the unstable intermediates in two ways. In the first, in order to measure the ratios of diastereoisomers, we used dimethylformamide,[9] which converts them into the corresponding nitriles **12** and **14**. Three of the four reactions appeared, as judged by ^{1}H NMR spectroscopy, to be highly diastereoselective, unexpectedly so in view of the discussion above. The result with the allylsilane **6a** is similar to that obtained by Taddei (60%; 80:20) using his trimethylsilyl analogue.[4] In the second, carried out to prove the relative stereochemistry of the products from the reaction with the allylsilanes **6**, we hydrolysed the intermediates to give the immediately crystalline and diastereoisomerically nearly pure primary amides **13**, showing that the apparent selectivity in these two cases was probably not caused by the diastereoisomers of **12a** and **12b** having unresolved ^{1}H NMR spectra. We proved the relative stereochemistry of the amides **13**, see below, but the configurations of the nitriles illustrated, by analogy, as **14**, remain in doubt, because we were unable to convert them with methyllithium into the corresponding ketones. Since one



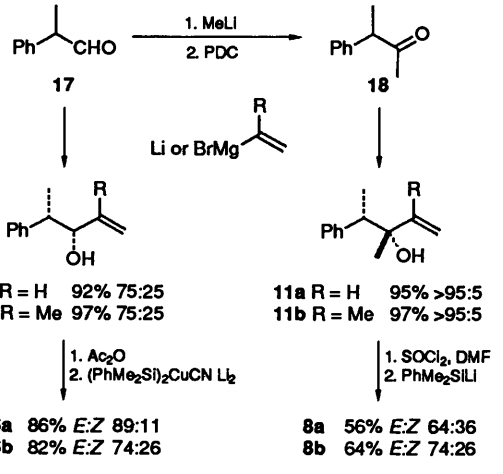


was produced with low diastereoselectivity, and the other was obtained only in low yield, we regard these two results as being suggestive rather than definitive. This leaves one result that does appear to be significant and unexplained, namely the high selectivity in the formation of **12a** from the very allylsilane **6a** that has hitherto been the least selective. Our explanation harks back to an aspect of the discussion in the preceding paper, where hydroboration, with a four-membered ring transition structure (**5** in the preceding paper), has the opposite diastereoselectivity from that shown by other electrophilic reactions. If CSI also reacts by way of a four-membered ring transition state, and if the *E*-isomer of **6a** reacts with a transition structure like **5** in the preceding paper, instead of reacting to some extent in the conformation with the methyl group eclipsing the double bond, it will cleanly give the nitrile **12a** (and the amide **13a**). The minor, *Z*-isomer can be expected, as usual, to be highly diastereoselective in the same sense, and the *E*- and *Z*-allylsilanes will support each other instead of subtracting from each other. The same argument explains the high selectivity for the reaction **8a** → **14a**, if **14a** is indeed the major diastereoisomer, as now seems even more likely.

We conclude from the reactions of these three electrophiles that the diastereotopic faces of a double bond, differentiated only by the difference between a phenyl group and a methyl group, can show surprisingly high diastereoselectivity in the best of these allylsilane reactions, better, in general, than the reactions of the enolates described in the preceding paper. In the best cases, even a small electrophile like a proton shows selectivity of 85:15, rising with the larger electrophiles, MCPBA and CSI, to 92:8 and >95:5, respectively.

Our final result is completely inexplicable at present. When we acetylated the allylsilanes **6**, we obtained the methyl ketones **15** with high diastereoselectivity, which appears to be *in the opposite sense* to that of all of the reactions described above. The reaction of the allylsilane **8b** was also highly diastereoselective, but we have not been able to determine the relative stereochemistry of the product **16b**. The allylsilane **8a** gave only a trace of anything that might have been the hoped for methyl ketone. The crude reaction mixture showed strong signals from the dimethylsilyl group, indicating that this allylsilane had been acetylated substantially at C-2, without subsequent loss of the silyl group. This is a type of reaction that has been seen before with allylsilanes having this substitution pattern.[3,10]

Synthesis of the Allylsilanes.—2-Phenylpropionaldehyde **17** was the starting material for all four allylsilanes. Its reaction with vinylmagnesium bromide and isopropenylmagnesium bromide gave the alcohols **10**, with diastereoselectivity in the sense of Cram's rule to the extent of 75:25 in both cases, and in favour of the isomers illustrated. The acetates of these alcohols reacted with our phenyldimethylsilyl cuprate reagent to give the allylsilanes **6** as mixtures of stereoisomers.[11] For the synthesis of the allylsilanes **8**, we converted the aldehyde into the ketone **18**, which we treated with vinylmagnesium bromide and isopropenyllithium to give the alcohols **11** with high diastereoselectivity, which we assume to have followed Cram's rule. Because these alcohols were difficult to acetylate, we made the allylsilanes by first converting the alcohols into the rearranged allylic chlorides, using thionyl chloride, and treating the chlorides with phenyldimethylsilylithium.[12] We have assigned the *E* stereochemistry to the major allylsilane by analogy with our own[11] and Smith's[12] work establishing that the *E* isomer is the major product in these types of reaction; unfortunately NOE experiments were inconclusive.

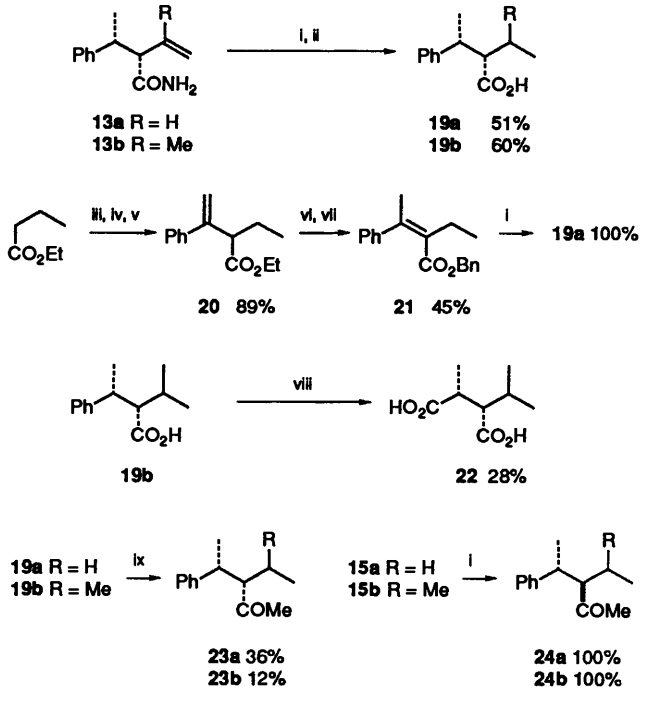


Proof of Relative Configuration of the Products.—Ozonolysis of a mixture rich (85:15) in the *minor* isomer (*i.e.* the diastereoisomer of **9b**) from the protodesilylation of the allylsilane **8b** gave a mixture rich (85:15) in the corresponding ketone (numbered **8a** in the preceding paper), readily recognised by its ^1H NMR spectrum.

The alcohols **10** were readily recognised, because they were the starting materials for the synthesis of the allylsilanes, and had been prepared by a reaction that could reasonably be trusted to have followed Cram's rule. We confirmed our stereochemical assignments to them by hydrogenation of the product mixtures from the Grignard reactions, to give mixtures of the known saturated alcohols,[13] authentic samples of which we also prepared by addition of ethyl- and isopropyl-magnesium halides to the same aldehyde **17**. It seems unlikely that the Grignard and isopropenyllithium reactions forming the alcohols **11** had not also obeyed Cram's rule, especially in view

of the fact that the reactions were conspicuously diastereoselective. Furthermore, there is the striking internal consistency that the major products **10** and **11** of the epoxidation reactions were, in all four cases, also the major products of the Grignard and isopropenyllithium reactions.

Hydrogenation of the amides **13**, followed by nitrosation,[14] gave the saturated carboxylic acids **19**. We prepared an authentic sample of the acid **19a** from ethyl butyrate by way of the esters **20** and **21**. An NOE experiment showed that the ester **21** was the *Z*-isomer, and the hydrogenation step was stereochemically clean and, therefore, very probably stereo-



Reagents: i, H_2, Pd/C; $NOBF_4$; iii, LDA; iv, PhCOMe; TsOH; vi, NaOEt; vii, BnOH, $Ti(OPr^i)_4$ cat.; viii, RuO_4; ix, MeLi

specifically *syn*. Taddei also proved the configuration of the major product **12a**.[4] We oxidised the acid **19b** to the known dicarboxylic acid **22**.[15]

We also converted the acids **19** into the corresponding methyl ketones **23** by treating them with methyllithium. Hydrogenation of the ketones **15** gave, as major products, the diastereoisomers **24** of these ketones, contaminated with enough of the minor isomers **23** for them to be recognisable as the products obtained from the acids **19**. There is a small possibility that the hydrogenation epimerised the ketones. We were not able to rule out this possibility, and do not at this stage want to make more of the anomalous stereochemistry of these acetylation reactions.

Experimental

Light petroleum refers to the fraction boiling between 30 and 40 °C.

Proto- and Deutero-desilylation of the Allylsilanes.—[^{1}H or ^{2}H]Acetic acid (1.2 mmol) was added to a solution of the allylsilane (1 mmol) and boron trifluoride (1.2 mmol) in dichloromethane (5 cm^3) at 0 °C under nitrogen. After 1–4 h, the solution was diluted with aqueous sodium hydrogen carbonate (5%; 10 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel (20 g) eluting with light petroleum to give the alkenes. The following alkenes were made by this method.

4-*Phenylpent*-1-*ene* (75%). R_f (light petroleum) 0.7; ν_{max}(film)/cm^{-1} 1640 (C=C); δ(250 MHz; $CDCl_3$) 7.33–7.14 (5 H, m, Ph), 5.7 (1 H, ddt, *J* 13, 9.5 and 7.5, C*H*=CH_2), 5.03–4.92 (2 H, m, C=CH_2), 2.78 (1 H, sextet, *J* 7, PhC*H*), 2.45–2.25 (2 H, m, CH_2C=C) and 1.25 (3 H, d, *J* 7, PhCH*Me*); *m*/*z* 146 (5%, M^+), 105 (100, PhCHMe), 79 (35, C_6H_7) and 77 (35, Ph) (Found: M^+, 146.1093. $C_{11}H_{14}$ requires *M*, 146.1096).

4-*Phenyl*[3-^{2}H]*pent*-1-*ene* **7a** (71%). R_f (light petroleum) 0.7; ν_{max}(film)/cm^{-1} 1640 (C=C); δ(250 MHz; $CDCl_3$) 7.34–7.16 (5 H, m, Ph), 5.76–5.65 (1 H, m, C*H*=CH_2), 5.04–4.93 (2 H, m, C=CH_2), 2.79 (1 H, quintet, *J* 7, PhC*H*), 2.4 (1 H, br t, *J* 7, C*H*D, major isomer), 2.27 (1 H, br t, *J* 7, C*H*D, minor isomer) and 1.25 (3 H, d, *J* 7, PhCH*Me*). The mass spectrum showed a ratio of peaks 147:146 to be >98%.

2-*Methyl*-4-*phenylpent*-1-*ene*[16] (85%). R_f (light petroleum) 0.72; ν_{max}(film)/cm^{-1} 1640 (C=C); δ_H(250 MHz; $CDCl_3$) 7.31–7.13 (5 H, m, Ph), 4.7 (1 H, s, C=CH_AH_B), 4.62 (1 H, s, C=CH_AH_B), 2.9 (1 H, sextet, *J* 7, PhC*H*), 2.34 (1 H, dd, *J* 14 and 7, CH_AH_B), 2.25 (1 H, dd, *J* 14 and 8, CH_AH_B), 1.68 (3 H, s, C=CMe) and 1.2 (3 H, d, *J* 7, PhCH*Me*); δ_C($CDCl_3$; 63 MHz) 147.5, 144.1, 128.3, 126.9, 125.9, 112.0, 46.9, 37.83, 22.3 and 21.6.

2-*Methyl*-4-*phenyl*[3-^{2}H]*pent*-1-*ene* **7b** (92%). R_f (light petroleum) 0.72; ν_{max}(film)/cm^{-1} 1640 (C=C); δ(250 MHz; $CDCl_3$) 7.32–7.14 (5 H, m, Ph), 4.71 (1 H, s, C=CH_AH_B), 4.63 (1 H, s, C=CH_AH_B), 2.90 (1 H, quintet, *J* 7, PhC*H*), 2.34 (1 H, br d, *J* 7, C*H*D, major isomer), 2.25 (1 H, br d, *J* 8, C*H*D, minor isomer), 1.68 (3 H, s, C=CMe) and 1.21 (3 H, d, *J* 7, PhCH*Me*); δ_C($CDCl_3$; 63 MHz) identical with that of the undeuteriated compound except for the signal at δ 46.5 (t, *J* 19). The mass spectrum showed a ratio of peaks 161:160 of 94:6.

3-*Methyl*-4-*phenylpent*-1-*ene* **9a** (75%). R_f (light petroleum) 0.70; ν_{max}(film)/cm^{-1} 1640 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*) and (3*RS*,4*RS*) 7.33–7.14 (5 H, m, Ph), 5.8–5.57 (1 H, m, C*H*=CH_2), 5.05–4.85 (2 H, m, C=CH_2), 2.7–2.28 (2 H, m, PhC*H*C*H*) and 1.24, 1.21, 0.97 and 0.82 (6 H, 4 × d, *J* 7, CH*Me*) (the peaks were well resolved, but it was not possible to assign which came from which isomer with any confidence, because they were present in such nearly equal amounts; the ratio was measured using the upfield pair of doublets); *m*/*z* 161 (3%, M^+) and 105 (100, PhCHMe) (Found: M^+, 160.1252. $C_{12}H_{16}$ requires *M*, 160.1267).

2,3-*Dimethyl*-4-*phenylpent*-1-*ene* **9b** (86%). R_f (light petroleum) 0.76; ν_{max}(film)/cm^{-1} 1640 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(major): 7.33–7.12 (5 H, m, Ph), 4.80 (1 H, br s, C=CH_AH_B), 4.76 (1 H, br s, C=CH_AH_B), 2.54 (1 H, dq, *J* 10.5 and 7, PhC*H*), 2.32 (1 H, dq, *J* 10.5 and 7, C=CCH), 1.73 (3 H, s, C=CMe), 1.13 (3 H, d, *J* 7, PhCH*Me*) and 0.75 (3 H, d, *J* 7, C=CCH*Me*); (3*RS*,4*RS*)(minor): 7.32–7.12 (5 H, m, Ph), 4.59 (1 H, br s, C=CH_AH_B), 4.54 (1 H, br s, C=CH_AH_B), (2 H, m, C=CH_2), 2.77 (1 H, quintet, *J* 7.5, PhC*H*), 2.38 (1 H, quintet, *J* 7.5, C=CCH), 1.61 (3 H, s, C=CMe), 1.2 (3 H, d, *J* 7 PhCH*Me*) and 1.04 (3 H, d, *J* 7, C=CCH*Me*); *m*/*z* 174 (5%, M^+) and 105 (100, PhCHMe) (Found: M^+, 174.1405. $C_{13}H_{18}$ requires *M*, 174.1408). Chromatography enabled us to enrich this mixture to obtain a sample with the isomers in a ratio of 15:85.

Epoxidation Reactions of the Allylsilanes.—The allylsilane (1 mmol), *m*-chloroperoxybenzoic acid (1.2 mmol) and disodium hydrogen phosphate (1.2 mmol) in dichloromethane (5 cm^3) were stirred at 0 °C for 1 h. The mixture was diluted with aqueous sodium hydrogen carbonate (5%; 10 cm^3) and extracted with ether (2 × 10 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude epoxysilane. The epoxysilane was treated with tetrabutylammonium fluoride (1 mmol) in THF (5 cm^3) at 20 °C for 2–4 h. The solution was diluted with water (10 cm^3) and

extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The products were chromatographed on silica gel (20 g) eluting with light petroleum–diethyl ether (99:1, v/v) to give the allyl alcohols. The following alcohols were made by this method.

4-*Phenylpent*-1-*en*-3-*ol* **10a** (71%). R_f (light petroleum–Et_2O, 7:3, v/v) 0.46; ν_{max}(film)/cm^{-1} 3400 (OH) and 1640 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(minor): 7.4–7.2 (5 H, m, Ph), 5.95–5.8 (1 H, m, C*H*=CH_2, detail not discernible), 5.35–5.1 (2 H, m, C=CH_2, detail not discernible), 4.15 (1 H, t, *J* 7, C*H*OH), 2.9 (1 H, quintet, *J* 7, PhC*H*), 1.8 (1 H, br s, OH) and 1.25 (3 H, d, *J* 7, PhCH*Me*); (3*RS*,4*RS*)(major): 7.4–7.2 (5 H, m, Ph), 5.79 (1 H, ddd, *J* 17, 10.5 and 6, C*H*=CH_2), 5.18 (1 H, dt, *J* 17 and 1.5, C=CH_AH_B), 5.10 (1 H, dt, *J* 10.5 and 1.5, C=CH_AH_B), 4.22 (1 H, tt, *J* 6 and 1.5, C*H*OH), 2.95 (1 H, quintet, *J* 6, PhC*H*), 1.8 (1 H, br s, OH) and 1.33 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 81.5; H, 8.6. $C_{11}H_{14}O$ requires C, 81.5; H, 8.70%).

2-*Methyl*-4-*phenylpent*-1-*en*-3-*ol* **10b** (85%). R_f (light petroleum–Et_2O, 7:3, v/v) 0.47, ν_{max}(film)/cm^{-1} 3350 (OH) and 1645 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(major): 7.4–7.2 (5 H, m, Ph), 4.90 (1 H, s, C=CH_AH_B), 4.8 (1 H, s, C=CH_AH_B), 4.2 (1 H, d, *J* 6, C*H*OH), 3.0 (1 H, quintet, *J* 7, PhC*H*), 1.7 (3 H, s, C=CMe), 1.65 (1 H, s, OH) and 1.3 (3 H, d, *J* 7, PhCH*Me*); (3*RS*,4*RS*)(minor): 7.4–7.2 (5 H, m, Ph), 4.98 (1 H, br s, C=CH_AH_B), 4.96 (1 H, br s, C=CH_AH_B), 4.1 (1 H, d, *J* 9, C*H*OH), 2.87 (1 H, dq, *J* 9 and 7, PhC*H*), 1.82 (3 H, s, C=CMe), 1.65 (1 H, s, OH) and 1.17 (3 H, d, *J* 7, PhCHMe) (Found: C, 81.7; H, 9.20. $C_{12}H_{16}O$ requires C, 81.8; H, 9.10%).

3-*Methyl*-4-*phenylpent*-1-*en*-3-*ol* **11a** (76%). R_f (light petroleum–Et_2O, 7:3, v/v) 0.49, ν_{max}(film)/cm^{-1} 3400 (OH) and 1640 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(minor): 7.32–7.18 (5 H, m, Ph), 5.93 (1 H, dd, *J* 11 and 17, C*H*=CH_2), 5.08 (1 H, dd, *J* 17 and 1, C=CH_AH_B), 5.05 (1 H, d, 5.5, *J* 11 and 1, C=CH_AH_B), 2.87 (1 H, q, *J* 7.2, PhC*H*), 1.46 (1 H, br s, OH), 1.31 (3 H, d, *J* 7.2, PhCH*Me*) and 1.22 (3 H, s, *Me*COH); (3*RS*,4*RS*)(major): 7.3–7.2 (5 H, m, Ph), 5.95 (1 H, dd, *J* 11 and 17, C*H*=CH_2), 5.20 (1 H, dt, *J* 17 and 1, C=CH_AH_B), 5.1 (1 H, dt, *J* 11 and 1.3, C=CH_AH_B), 2.18 (1 H, q, *J* 7.2, PhC*H*), 1.46 (1 H, br s, OH), 1.29 (3 H, d, *J* 7.2, PhCH*Me*) and 1.2 (3 H, s, MeCOH) (Found: C, 82.0; H, 9.05. $C_{12}H_{16}O$ requires C, 81.8; H, 9.10%).

2,3-*Dimethyl*-4-*phenylpent*-1-*en*-3-*ol* **11b** (81%). R_f (light petroleum–Et_2O, 7:3, v/v) 0.45; ν_{max}(film)/cm^{-1} 3400 (OH) and 1640 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(major): 7.32–7.21 (5 H, m, Ph), 5.13 (1 H, br s, C=CH_AH_B), 4.90 (1 H, br s, C=CH_AH_B), 2.92 (1 H, q, *J* 7, PhC*H*), 1.81 (3 H, s, C=CMe), 1.81 (3 H, s, C=CMe) 1.4 (1 H, s, OH), 1.2 (3 H, d, *J* 7, PhCH*Me*) and 1.07 (3 H, s, *Me*COH); (3*RS*,4*RS*)(minor): 7.31–7.21 (5 H, m, Ph), 4.77 (2 H, br s, C=CH_2), 3.04 (1 H, q, *J* 7.3, PhC*H*), 1.79 (3 H, s, C=CMe), 1.43 (1 H, br s, OH) and 1.28 (6 H, m, remainder) (Found: C, 82.1; H, 9.75. $C_{13}H_{18}O$ requires C, 82.1; H, 9.5%).

Reaction of the Allylsilanes with Chlorosulfonyl Isocyanate (CSI).—Chlorosulfonyl isocyanate (1.2 mmol) was added to a solution of the allylsilane (1 mmol) in carbon tetrachloride (3 cm^3) at 0 °C under nitrogen. After 30 min, the solvent was removed under a stream of nitrogen and the residue was treated in one of the following ways (A) or (B). (A) The residue was dissolved in DMF (1 cm^3) and kept at 50 °C for 10 min. The solution was diluted with water (10 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The product was chromatographed on silica gel (15 g) eluting with light petroleum–Et_2O (99:1). The following nitriles were made by this method.

(2RS,1'SR)-2-(1-*Phenylethyl*)*but*-3-*enonitrile* **12a** (79%). A low-melting solid; R_f (light petroleum–Et_2O, 9:1, v/v) 0.33; ν_{max}(Nujol)/cm^{-1} 2250 (CN) and 1640 (C=C); δ(250 MHz; $CDCl_3$) 7.37–7.22 (5 H, m, Ph), 5.61 (1 H, ddd, *J* 17, 10 and 5.5, C*H*=CH_2), 5.43 (1 H, dt, *J* 17 and 1, C=CH_AH_B), 5.27 (1 H, dt, *J* 10 and 1, C=CH_AH_B), 3.48 (1 H, ddt, *J* 6, 5.5 and 1, CHCN), 3.0 (1 H, quintet, *J* 7, PhC*H*) and 1.45 (3 H, d, *J* 7, PhCH*Me*); *m*/*z* 171 (2%, M^+) and 105 (100, PhCHMe) (Found: M^+, 171.1057. $C_{12}H_{13}N$ requires *M*, 171.1048).

(2RS,1'RS)-3-*Methyl*-2-(1-*phenylethyl*)*but*-3-*enonitrile* **12b** (82%). A low-melting solid; R_f (light petroleum–Et_2O, 9:1, v/v) 0.35; ν_{max}(Nujol)/cm^{-1} 2250 (CN) and 1640 (C=C); δ(250 MHz; $CDCl_3$) 7.36–7.21 (5 H, m, Ph), 4.99 (1 H, br s, C=CH_AH_B), 4.95 (1 H, br s, C=CH_AH_B), 3.35 (1 H, d, *J* 7, CHCN), 3.16 (1 H, quintet, *J* 7, PhC*H*), 1.78 (3 H, s, C=CMe) and 1.45 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 84.0; H, 8.4; N, 7.35. $C_{13}H_{15}N$ requires C, 84.3; H, 8.10; N, 7.55%).

(2RS,1'RS)-2-*Methyl*-2-(1-*phenylethyl*)*but*-3-*enonitrile* **14a** (40%). A low-melting solid; R_f (light petroleum–Et_2O, 9:1, v/v) 0.37; ν_{max}(Nujol)/cm^{-1} 2250 (CN) and 1640 (C=C); δ(250 MHz; $CDCl_3$) 7.35–7.22 (5 H, m, Ph), 5.65 (1 H, dd, *J* 17 and 9, C*H*=CH_2), 5.54 (1 H, dd, *J* 17 and 1.5, C=CH_AH_B), 5.29 (1 H, dd, *J* 9 and 1.5, C=CH_AH_B), 2.7 (1 H, q, *J* 7, PhC*H*), 1.4 (3 H, d, *J* 7, PhCH*Me*) and 1.2 (3 H, s, MeCCN); *m*/*z* 185 (5%, M^+) and 105 (100, PhCHMe) (Found: M^+, 185.1204. $C_{13}H_{15}N$ requires *M*, 185.1214). The minor, (3*RS*,4*SR*)-isomer was just visible with signals at: δ 2.95 (q, *J* 7) and 1.45 (d, *J* 7).

(2RS,1'SR)-2,3-*Dimethyl*-2-(1-*phenylethyl*)*but*-3-*enonitrile* **14b** (81%). A low-melting solid; R_f (light petroleum–Et_2O, 9:1, v/v) 0.35; ν_{max}(Nujol)/cm^{-1} 2250 (CN) and 1650 (C=C); δ(250 MHz; $CDCl_3$) 7.38–7.24 (5 H, m, Ph), 5.40 (1 H, br s, C=CH_AH_B), 5.08 (1 H, br s, C=CH_AH_B), 2.88 (1 H, q, *J* 7, PhC*H*), 1.83 (3 H, br s, C=CMe), 1.35 (3 H, d, *J* 7, PhCH*Me*), and 1.20 (3 H, s, MeCCN); *m*/*z* 199 (6%, M^+) and 105 (100, PhCHMe) (Found: M^+, 199.1360. $C_{14}H_{17}N$ requires *M*, 199.1360). The minor, (3*RS*,4*RS*)-isomer was clearly visible with signals at: δ 4.98 (br s), 5.84 (br s), 2.99 (q, *J* 7), 1.70 (br s), 1.54 (s) and 1.40 (d, *J* 7).

(B) The residue was dissolved in a mixture of acetone (2.5 cm^3), water (1 cm^3) and hydrochloric acid (3 mol dm^{-3}; 0.2 cm^3) and the solution was stirred for 30 min at 20 °C. The solvent was then evaporated under reduced pressure and the residue purified by passage through silica gel (10 g), with light petroleum followed by ethyl acetate as eluent. The following amides were made by this method.

(2RS,1'SR)-2-(1-*Phenylethyl*)*but*-3-*enamide* **13a** (52%). Prisms, m.p. 180–182 °C (from toluene), R_f (EtOAc–hexane, 2:1, v/v) 0.50; ν_{max}(Nujol)/cm^{-1} 3380, 3190 (NH_2) and 1640 (C=O); δ(250 MHz; CD_3COCD_3) 7.3–7.1 (5 H, m, Ph), 7.0 (1 H, br s, CONH_AH_B), 6.4 (1 H, br s, CONH_AH_B), 5.63 (1 H, ddd, *J* 16, 10 and 8, C*H*=CH_2), 4.84 (1 H, br d, *J* 16, C=CH_AH_B), 4.79 (1 H, br d, *J* 10, C=CH_AH_B), 3.17–3.05 (2 H, m, PhC*HCH*) and 1.25 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 76.3; H, 8.0; N, 7.4. $C_{12}H_{15}NO$ requires C, 76.2; H, 7.90; N, 7.40%). The minor, (2*RS*,1'*RS*)-isomer was just visible with signals at δ 5.85 (dt, *J* 16 and 8), 5.18 (br d, *J* 16), 5.13 (br d, *J* 10) and 1.20 (d, *J* 7). The ratio of major to minor isomer was 95:5.

(2RS,1'RS)-3-*Methyl*-2-(1-*phenylethyl*)*but*-3-*enamide* **13b** (57%). Prisms, m.p. 170–172 °C (from toluene); R_f(EtOAc–hexane, 2:1, v/v) 0.50; ν_{max}(Nujol)/cm^{-1} 3400, 3200 (NH_2) and 1640 (C=O); δ(250 MHz; CD_3COCD_3) 7.28–7.09 (5 H, m, Ph), 6.9 (1 H, br s, CONH_AH_B), 6.3 (1 H, br s, CONH_AH_B), 4.77 (1 H, quintet, *J* 0.7, C=CH_AH_B), 4.57 (1 H, quintet, *J* 1.5, C=CH_AH_B), 3.35 (1 H, d, *J* 7, CHCO), 3.29 (1 H, dq, *J* 11 and 7, PhC*H*), 1.57 (3 H, t, *J* 1, C=CMe) and 1.21 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 76.8; H, 8.25; N, 6.85. $C_{13}N_{17}NO$ requires C, 76.8; H, 8.40; N, 6.90%).

Acetylation of the Allylsilanes.—Titanium tetrachloride (1 mmol) was added to a solution of acetyl chloride (1.5 mmol) in dichloromethane (3 cm^3) at −78 °C under nitrogen. After 5

min, a pre-cooled solution of allylsilane (1 mmol) in dichloromethane (2 cm^3) was added. After a further 5 min, the mixture was diluted with aqueous sodium hydrogen carbonate (5%; 10 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The product was chromatographed on silica gel (20 g) eluting with light petroleum–diethyl ether (99:1) to give the enones. The following ketones were made by this method:

3-(1-*Phenylethyl*)*pent*-4-*en*-2-*one* **15a** (84%). A low-melting solid; R_f (light petroleum–Et_2O, 9:1, v/v) 0.48; ν_{max}(Nujol)/cm^{-1} 1705 (C=O) and 1625 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,1′*SR*)(minor): 7.3–7.14 (5 H, m, Ph), 5.55 (1 H, dt, *J* 17.5 and 9.5, C*H*=CH_2), 4.96 (2 H, m, C=CH_2), *ca.* 3.33 (1 H, m, CHCO), *ca.* 3.13 (1 H, m, PhC*H*), 2.17 (3 H, s, COMe) and 1.22 (3 H, d, *J* 7, PhCH*Me*), with the signals at 3.33 and 3.13 incompletely resolved and largely buried under the signals from the major isomer; (3*RS*,1′*RS*)(major): 7.3–7.14 (5 H, m, Ph), 5.76 (1 H, dt, *J* 17.5 and 9.5, C*H*=CH_2), 5.23 (1 H, br d, *J* 9.5, C=CH_AH_B), 5.21 (1 H, br d, *J* 17.5, C=CH_AH_B), 3.35 (1 H, t, *J* 10, CHCO), 3.12 (1 H, dq, *J* 10 and 7, PhC*H*), 1.83 (3 H, s, COMe) and 1.20 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 83.3; H, 8.6. $C_{13}H_{16}O$ requires C, 83.0; H, 8.5%).

(3RS,1′SR)-4-*Methyl*-3-(1-*phenylethyl*)-*pent*-4-*en*-2-*one* **15b** (77%). A low-melting solid; R_f (light petroleum–Et_2O, 9:1, v/v) 0.43; ν_{max}(Nujol)/cm^{-1} 1710 (C=O) and 1640 C=C); δ(250 MHz; $CDCl_3$) 7.29–7.15 (5 H, m, Ph), 5.06 (1 H, br s, C=CH_AH_B), 5.03 (1 H, br s, C=CH_AH_B), 3.5 (1 H, d, *J* 11, CHCO), 3.25 (1 H, dq, *J* 11 and 7, PhC*H*), 1.85 (3 H, s, COMe), 1.74 (3 H, s, C=CMe) and 1.13 (3 H, d, *J* 7, PhCH*Me*); *m*/*z* 202 (6%, M^+) and 105 (100, PhCHMe) (Found: M^+, 202.1351. $C_{14}H_{18}O$ requires *M*, 202.1357). The minor, (2*RS*,1′*RS*)-isomer is probably responsible for the just visible signals at: δ 5.8 (br s), 1.82 (s), 1.62 (s) and 1.17 (d, *J* 7). A substantial by-product from this reaction, obtained in variable yield when it was carried out by adding the titanium tetrachloride to a mixture of the allylsilane and acetyl chloride, was the mixture of the geometrically isomeric enones, 4-*methyl*-6-*phenylhept*-4-*en*-2-*ones*, regioisomeric with the ketone **15b**, R_f (light petroleum–Et_2O, 9:1, v/v) 0.18; ν_{max}(film)/cm^{-1} 1710 (C=O); δ(250 MHz; $CDCl_3$) (*E*)(major): 7.32–7.14 (5 H, m, Ph), 5.43 (1 H, br d, *J* 9, CH=C), 3.70 (1 H, dq, *J* 9 and 7, PhC*H*), 3.05 (2 H, s, $COCH_2$), 2.09 (3 H, s, COMe), 1.68 (3 H, br s, C=CMe) and 1.33 (3 H, d, *J* 7, PhCH*Me*); (*Z*)-minor): 7.32–7.14 (5 H, m, Ph), 5.56 (1 H, br d, *J* 8, CH=C), 3.60 (1 H, m, incompletely resolved from the signal of the major isomer, PhC*H*), 3.17 (2 H, s, $COCH_2$), 2.04 (3 H, s, COMe), 1.72 (3 H, br s, C=CMe) and 1.32 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 83.3; H, 9.15. $C_{14}H_{18}O$ requires C, 83.2; H, 8.90%). This product is probably a consequence of the titanium tetrachloride attacking the allylsilane first, followed by the attack of acetyl chloride on the allyltitanium intermediate.[2] This pitfall in allylsilane chemistry is avoided almost completely by the alternative recipe given above.

3,4-*Dimethyl*-3-(1-*phenylethyl*)*pent*-4-*en*-2-*one* **16b** (36%). R_f (light petroleum–Et_2O, 9:1, v/v) 0.30; ν_{max}(film)/cm^{-1} 1705 (C=O) and 1630 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,1′*SR*) (presumed only by analogy): 7.25–7.15 (5 H, m, Ph), 5.32 (1 H, s, C=CH_AH_B), 5.31 (1 H, s, C=CH_AH_B), 3.37 (1 H, q, *J* 7, PhC*H*), 1.85 (3 H, s, COMe), 1.35 (3 H, d, *J* 7, PhCH*Me*), 1.22 (3 H, s, C=CMe) and 1.08 (3 H, s, CMeCO) (Found: C, 83.6; H, 9.5. $C_{15}H_{20}O$ requires C, 83.3; H, 9.25%), with no trace of the signals from the diastereoisomer.

3-*Phenylbutan*-2-*one* **18**.—2-Phenylpropionaldehyde (5 g, 37 mmol) in THF (10 cm^3) was added to a solution of methyllithium (1.6 mol dm^{-3} solution in Et_2O, 25 cm^3; 40 mmol) in THF (40 cm^3) at −5 °C over 30 min. A standard aqueous work-up gave the alcohols[17] (5.35 g, 96%), b.p. 56–58 °C/0.07 mmHg. These alcohols (4.5 g, 30 mmol), pyridinium dichromate (11.3 g, 60 mmol) were stirred in dimethylformamide (60 cm^3) at room temperature for 4 h. A standard aqueous work-up and chromatography (SiO_2, light petroleum–Et_2O, 98:2, v/v) gave the ketone[17] (3.96 g, 89%).

Synthesis of the Allyl Alcohols **10** *and* **11**.—The aldehyde **17** or the ketone **18** (1 mmol) in THF (5 cm^3) was added dropwise to a solution of vinylmagnesium bromide[18] or propen-2-ylmagnesium bromide[19] (1.5 mmol) in THF (6 cm^3) at 0 °C under nitrogen or argon. After 15 min, the mixture was diluted with water (5 cm^3) and aqueous ammonium chloride (5 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The following alcohols were made by this method: 4-phenylpent-1-en-3-ol **10a** (92%), 2-methyl-4-phenylpent-1-en-3-ol **10b** (97%) and 3-methyl-4-phenylpent-1-en-3-ol **11a** (95%). A similar preparation, but using propen-2-yllithium, prepared by treating 2-bromopropene (1 mmol) with *tert*-butyllithium (2 mmol) in THF (5 cm^3) at −78 °C under nitrogen for 1.5 h and then allowing it to warm to 0 °C, gave 2,3-dimethyl-4-phenylpent-1-en-3-ol **11b** (97%). All four diastereoisomeric pairs of alcohols had spectroscopic data identical with those reported above, but in different ratios, as given in the text.

Acetylation of Alcohols.—Triethylamine (1.1 mmol) and acetic anhydride (1.1 mmol) were added to the alcohol (1 mmol) and 4-dimethylaminopyridine (0.2 mmol) in dry dichloromethane (5 cm^3), and the mixture was stirred for 16 h. The solvent was evaporated under reduced pressure and the residue taken up in ether (10 cm^3). The organic phase was washed with aqueous hydrochloric acid (1 mol dm^{-3}; 5 cm^3) and aqueous sodium hydrogen carbonate (5%; 10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The following aceates were made by this method.

4-*Phenylpent*-1-*en*-3-*yl acetate* (92%). R_f (light petroleum–Et_2O, 7:3, v/v) 0.61; ν_{max}(film)/cm^{-1} 1740 (C=O) and 1645 (C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(minor): 7.32–7.17 (5 H, m, Ph), 5.74 (1 H, ddd, *J* 17, 10 and 6, C*H*=CH_2), 5.39 (1 H, tt, *J* 6 and 1, C*H*OAc), 5.25 (1 H, dt, *J* 17 and 1, C=CH_AH_B), 5.22 (1 H, dt, *J* 10 and 1, C=CH_AH_B), 3.05 (1 H, m, PhC*H*, obscured by the signal of the major isomer), 1.91 (3 H, s, COMe) and 1.27 (3 H, d, *J* 7, PhCH*Me*); (3*RS*,4*RS*)(major): 7.32–7.17 (5 H, m, Ph), 5.63 (1 H, ddd, *J* 17, 10.5 and 6, C*H*=CH_2), 5.39 (1 H, tt, *J* 6 and 1, C*H*OAc), 5.12 (1 H, dt, *J* 17 and 1.3, C=CH_AH_B), 5.09 (1 H, dt, *J* 10.5 and 1.3, C=CH_AH_B), 2.99 (1 H, quintet, *J* 7, PhC*H*), 2.08 (3 H, s, COMe) and 1.31 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 76.7; H, 7.7. $C_{13}H_{16}O_2$ requires C, 76.5; H, 7.80%).

2-*Methyl*-4-*phenylpent*-1-*en*-3-*yl acetate* (92%). R_f (light petroleum–Et_2O, 7:3, v/v) 0.57; ν_{max}(film)/cm^{-1} 1745 (C=O) and 1640 C=C); δ(250 MHz; $CDCl_3$) (3*RS*,4*SR*)(major): 7.27–7.17 (5 H, m, Ph), 5.28 (1 H, d, *J* 8, C*H*OAc), 4.78 (2 H, br s, C=CH_2), 3.04 (1 H, quintet, *J* 7.2, PhC*H*), 2.06 (3 H, s, COMe), 1.61 (3 H, s, C=CMe) and 1.28 (3 H, d, *J* 7, PhCH*Me*); (3*RS*,4*RS*)(minor): 7.27–7.17 (5 H, m, Ph), 5.32 (1 H, d, *J* 8, C*H*OAc), 5.03 (1 H, br s, C=CH_AH_B), 4.97 (1 H, br s, C=CH_AH_B), 3.0 (1 H, m, PhC*H*, obscured by the signal of the major isomer), 1.8 (3 H, s, COMe), 1.73 (3 H, s, C=CMe) and 1.19 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 77.1; H, 8.1. $C_{14}H_{18}O_2$ requires C, 77.1; H, 8.30%).

Preparation of the Allylsilanes from Allyl Acetates.—Dimethyl(phenyl)silyllithium[20] (2 mmol) in THF (5 cm^3) was added to a suspension of copper(I) cyanide (1 mmol) in ether (10 cm^3) at 0 °C under nitrogen. After 20 min, the mixture was cooled to −23 °C and the allyl acetates (1 mmol) in ether (5 cm^3) were added with rapid stirring. After 20 min, the mixture was diluted with aqueous ammonium chloride (20 cm^3) and extracted with ether (2 × 10 cm^3). The extracts were dried

($MgSO_4$) and evaporated under reduced pressure. The product was chromatographed on silica gel (20 g) eluting with light petroleum. The following allylsilanes were made by this method.

Dimethyl(phenyl)-4-phenylpent-2-enylsilane **6a** (93%). R_f (light petroleum) 0.27; ν_{max}(film)/cm^{-1} 1245 (SiMe), 1110 (SiPh) and 960 (*E*-CH=CH); δ(250 MHz; $CDCl_3$) (*E*)(major): 7.56–7.2 (10 H, m, 2 × Ph), 5.55 (2 H, m, CH=CH), 3.45 (1 H, quintet, *J* 7, PhC*H*), 1.73 (2 H, m, CH_2), 1.35 (3 H, d, *J* 7, PhCH*Me*) and 0.32 (6 H, s, $SiMe_2$); (*Z*)(minor): 7.6–7.2 (10 H, m, 2 × Ph), 5.55 (2 H, m, CH=CH), 3.75 (1 H, m, PhC*H*), 1.9 (2 H, m, CH_2), 1.30 (3 H, d, *J* 7, PhCH*Me*) and 0.36 (6 H, s, $SiMe_2$) (Found: C, 81.2; H, 8.6. $C_{19}H_{24}Si$ requires C, 81.4; H, 8.60%).

Dimethyl(phenyl)-2-methyl-4-phenylpent-2-enylsilane **6b** (89%). R_f (light petroleum) 0.23; ν_{max}(film)/cm^{-1} 1250 (SiMe) and 1115 (SiPh); δ(250 MHz; $CDCl_3$) (*E*)(major): 7.56–7.14 (10 H, m, Ph), 5.23 (1 H, d, *J* 10, CH=C), 3.46 (1 H, dq, *J* 10 and 7, PhC*H*), 1.9 (1 H, d, *J* 17, $SiCH_AH_B$), 1.75 (1 H, d, *J* 17, $SiCH_AH_B$), 1.65 (3 H, d, *J* 1.5, C=CMe), 1.22 (3 H, d, *J* 7, PhCH*Me*), 0.33 (3 H, s, $SiMe_AMe_B$) and 0.31 (3 H, s, $SiMe_AMe_B$); (*Z*)(minor); 7.56–7.14 (10 H, m, Ph), 5.12 (1 H, d, *J* 10, CH=C), 3.66 (1 H, dq, *J* 10 and 7, PhC*H*), 1.76–1.75 (2 H, m, CH_2Si), 1.57 (3 H, d, *J* 1, C=CMe), 1.28 (3 H, d, *J* 7, PhCHMe), 0.29 (3 H, s, $SiMe_AMe_B$) and 0.28 (3 H, s, $SiMe_AMe_B$) (Found: C, 81.7; H, 8.75. $C_{20}H_{26}Si$ requires C, 81.6; H, 8.85%).

Preparation of the Allylsilanes by way of the Allyl Chlorides.—The allyl alcohol (1 mmol), thionyl chloride (1.5 mmol) and DMF (2 drops) in ether (3 cm^3) were stirred under a nitrogen atmosphere for 16 h. The mixture was diluted with water (10 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was taken up in light petroleum and filtered through silica gel (10 g). The solvent was evaporated under reduced pressure to give the crude allyl chloride. Dimethyl(phenyl)-silyllithium (1.2 mmol) in THF (5 cm^3) was added dropwise to a solution of the allyl chloride in ether (5 cm^3) at −78 °C under nitrogen. After 15 min, the mixture was diluted with water and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The allylsilanes were purified by column chromatography on silica gel (20 g) eluting with light petroleum. The following allylsilanes were made by this method.

Dimethylphenyl(3-methyl-4-phenylpent-2-enyl)silane **8a** (56%). R_f (light petroleum) 0.26; ν_{max}(film)/cm^{-1} 1245 (SiMe) and 1115 (SiPh); δ(250 MHz; $CDCl_3$) (*E*)(major): 7.57–7.17 (10 H, m, 2 × Ph), 5.39 (1 H, br t, *J* 8.5, CH=C), 3.38 (1 H, t, *J* 7, PhC*H*), 1.70 (2 H, d, *J* 8.5, CH_2Si), 1.34 (3 H, br s, C=CMe), 1.32 (3 H, d, *J* 7, PhCHMe) and 0.29 (6 H, s, $SiMe_2$); (*Z*)(minor): 7.57–7.17 (10 H, m, Ph), 5.22 (1 H, t, *J* 8.5, CH=C), 4.0 (1 H, t, *J* 7, PhC*H*), 1.93 (1 H, dd, *J* 14.5 and 8.5, $SiCH_AH_B$), 1.78 (1 H, d, *J* 14.5 and 8.5, $SiCH_AH_B$), 1.46 (3 H, br s, C=CMe), 1.27 (3 H, d, *J* 7, PhCH*Me*), and 0.33 (6 H, s, $SiMe_2$) (Found: C, 81.8; H, 8.75. $C_{20}H_{26}Si$ requires C, 81.6; H, 8.85%).

Dimethylphenyl(2,3-dimethyl-4-phenylpent-2-enyl)silane **8b** (64%). R_f (light petroleum) 0.25; ν_{max}(film)/cm^{-1} 1240 (SiMe) and 1115 (SiPh); δ(250 MHz; $CDCl_3$) (*E*)(major): 7.58–7.16 (10 H, m, 2 × Ph), 4.12 (1 H, q, *J* 7, PhC*H*), 1.8 (2 H, s, CH_2Si), 1.75 (3 H, s, $SiCH_2CMe$), 1.32 (3 H, d, *J* 7, PhCH*Me*), 1.25 (3 H, s, PhCHC*Me*), 0.339 (3 H, s, $SiMe_AMe_B$) and 0.333 (3 H, s, $SiMe_AMe_B$); (*Z*)(minor: 7.58–7.16 (10 H, m, 2 × Ph), 3.95 (1 H, q, *J* 7, PhC*H*), 1.64 (3 H, s, $SiCH_2CMe$), 1.41 (3 H, s, PhCHC*Me*), 1.20 (3 H, d, *J* 7, PhCH*Me*), 0.373 (3 H, s, $SiMe_AMe_B$) and 0.368 (3 H, s, $SiMe_AMe_B$) (Found: C, 82.1; H, 9.25. $C_{21}H_{28}Si$ requires C, 81.8; H, 9.10%). The singlet for the CH_2Si signal of the minor isomer must be obscured under one of the signals from the major isomer. Irradiation at the frequency of the signal at δ 1.75 causes an increase in intensity in the signals at δ 4.12 and 1.25. A by-product from this reaction was the diene, *2-methyl-3-methylene-4-phenylpent-1-ene* (15%); R_f (light petroleum) 0.36; ν_{max}(film)/cm^{-1} 1610 (C=C); δ(250 MHz; $CDCl_3$) 7.32–7.15 (5 H, m, Ph), 5.37, 5.13, 5.04 and 4.91 (1 H, each s, 2 × C=CH_2), 3.90 (1 H, q, *J* 7, PhC*H*), 1.90 (3 H, s, C=CMe) and 1.42 (3 H, d, *J* 7, PhCH*Me*) (Found: C, 90.5; H, 9.35. $C_{13}H_{16}$requires C, 90.7; H, 9.30%).

Ozonolysis of the Mixture of Alkenes **9b**.—Ozone was passed through a solution of the alkene **9b** and its diastereoisomer (15:85, 53 mg, 0.3 mmol) in methanol (0.5 cm^3) and dichloromethane (2.5 cm^3) containing sodium hydrogen carbonate (25 mg) at −78 °C until a permanent blue colour persisted. Nitrogen was passed through the mixture for 15 min after which the solvent was evaporated under reduced pressure. The residue was diluted with water (5 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were combined and stirred with hydrochloric acid (1 mol dm^{-3}; 10 cm^3) for 5 h. The organic layer was separated, washed with water (5 cm^3), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (10 g) eluting with light petroleum–diethyl ether (99:1, v/v) to give the ketones (34 mg, 64%) in the ratio (3*RS*,4*SR*):(3*RS*,4*RS*) of 15:85, as judged by the singlets at δ 2.18 and 1.85, respectively, in the ^1H NMR spectrum (see preceding paper).

2-Phenylpentan-3-ols.—The unsaturated alcohols **10a** (0.2 g, 1.2 mmol), derived from the aldehyde **17** in a ratio of 75:25, were stirred with rhodium on alumina (50 mg) in ethyl acetate (5 cm^3) under hydrogen at room temperature and pressure for 2 h. The catalyst was filtered off and the filtrate was evaporated under reduced pressure to give the alcohols[13] (0.2 g, 100%). GC (Carbowax 20 M column, 130 °C, carrier flow 300 kp) retention times for the two alcohols were (2*RS*,3*SR*): 17 min (25%) and (2*RS*,3*RS*): 22 min (75%). An authentic sample of the same pair of alcohols,[13] in a ratio (GC) of 25:75, respectively, was also prepared (0.24 g, 98%) from 2-phenylpropionaldehyde (0.2 g, 1.5 mmol) in ether (2 cm^3) with ethylmagnesium bromide (2 mmol) in ether (5 cm^3) at room temperature for 10 min.

2-Methyl-4-phenylpentan-2-ols.—The unsaturated alcohols **10b** (80 mg, 0.4 mmol), derived from the ketone **18** in a ratio of 75:25, were stirred with rhodium on alumina (20 mg) in ethyl acetate (5 cm^3) under hydrogen at ambient temperature and pressure for 2 h. The catalyst was filtered off and the filtrate was evaporated under reduced pressure to give the alcohols[13] (75 mg, 94%). GC, as above, gave retention times for the two alcohols (2*RS*,3*SR*): 12 min (25%) and (2*RS*,3*RS*): 16 min (75%). An authentic sample of the same pair of alcohols,[13] in a ratio (GC) of 15:85, respectively, was also prepared (0.66 g, 78%) from 2-phenylpropionaldehyde (0.5 g, 3.7 mmol) in ether (25 cm^3) with isopropylmagnesium chloride (7 mmol) in ether (25 cm^3) at 0 °C under nitrogen for 15 min.

(2RS,1′SR)-2-(*1-Phenylethyl*)*butanamide.*—The unsaturated amide **13a** (0.5 g, 2.6 mmol) was stirred in ethyl acetate (20 cm^3) with palladium on carbon (5%; 0.1 g) under hydrogen at room temperature and pressure for 1 h. The catalyst was filtered off and the filtrate evaporated under reduced pressure to give the *amide* (0.4 g, 80%) as needles, m.p. 130–132 °C (from toluene); R_f (EtOAC–hexane, 2:1, v/v) 0.45; ν_{max}(Nujol)/cm^{-1} 3380 and 3190 (NH_2) and 1640 (C=O); δ(250 MHz; $CDCl_3$) 7.33–7.14 (5 H, m, Ph), 5.7 (1 H, br s, $CONH_AH_B$), 5.5 (1 H, br s, $CONH_AH_B$), 2.88 (1 H, dq, *J* 7 and 10, PhC*H*), 2.2–2.1 (1 H, dt, *J* 4 and 10, CHCO), 1.21 (1 H, tq, *J* 10 and 7, CH_AH_B), 1.3–1.1 (1 H, ddq, *J* 10, 7 and 4, CH_AH_B), 1.27 (3 H, d, *J* 7, PhCH*Me*)

and 0.81 (3 H, t, *J* 7.3, CH_2Me) (Found: C, 75.7; H, 9.10; N, 7.50. $C_{12}H_{17}NO$ requires C, 75.4; H, 8.90; N, 7.30%).

(2RS,1'SR)-3-*Methyl*-2-(1-*phenylethyl*)*butanamide*.—The unsaturated amide **13b** (0.7 g, 3.4 mmol) was hydrogenated in the same way for 2 h, to give the *amide* (0.59 g, 84%) as needles, m.p. 158–160 °C (from toluene); R_f (EtOAc–hexane, 2:1, v/v) 0.50; ν_{max}(Nujol)/cm^{-1} 3380 and 3190 (NH_2) and 1640 (C=O); δ(250 MHz; CD_3COCD_3) 7.33–7.14 (5 H, m, Ph), 6.8 (1 H, br s, $CONH_AH_B$), 6.3 (1 H, br s, $CONH_AH_B$), 3.1 (1 H, dq, *J* 10.5 and 7, PhC*H*), 2.47 (1 H, dd, *J* 4 and 10.5, CHCO), 1.50 (1 H, d septet, *J* 4 and 7, C*H*Me_2), 1.22 (3 H, d, *J* 7, PhCH*Me*), 0.90 (3 H, d, *J* 7, CHMe_AMe$_B$) and 0.88 (3 H, d, *J* 7, CHMe$_A$$Me_B$) (Found: C, 75.9; H, 9.2; N, 7.0. $C_{13}N_{19}NO$ requires C, 76.1; H, 9.25; N, 6.80%).

(2RS,1'SR)-2-(1-*Phenylethyl*)*butanoic Acid* **19a**—The amide derived from **13a** (0.32 g, 1.7 mmol) and nitronium tetrafluoroborate (0.33 g, 2.5 mmol) in dry acetonitrile (5 cm^3) were kept at 70 °C for 15 min. The mixture was diluted with water (10 cm^3) and aqueous sodium carbonate (3 mol dm^{-3}, 10 cm^3) and extracted with ethyl acetate (10 cm^3). The aqueous extracts were acidified with hydrochloric acid solution (3 mol dm^{-3}) and extracted with ethyl acetate (2 × 10 cm^3). The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the *acid* (0.21 g, 64%) as a low-melting solid; R_f (EtOAc) 0.70; ν_{max}(Nujol)/cm^{-1} 1710 (C=O); δ(250 MHz; $CDCl_3$) 7.34–7.15 (5 H, m, Ph), 2.90 (1 H, dq, *J* 7 and 10.5, PhC*H*), 2.47 (1 H, dt, *J* 4 and 10.5, CHCO), 1.51–1.20 (2 H, m, CH_2Me), 1.30 (3 H, d, *J* 7, PhCH*Me*) and 0.83 (3 H, t, *J* 7.5, CH_2Me); *m*/*z* 192 (10%, M$^+$) and 105 (100, PhCHMe) (Found: M$^+$, 192.1147. $C_{12}H_{16}O_2$ requires *M*, 192.1150).

(2RS,1'SR)-3-*Methyl*-2-(1-*phenylethyl*)*butanoic Acid* **19b**.—The amide derived from **13b** (0.62 g, 3 mmol) was similarly hydrolysed to give the *acid* (0.44 g, 72%) as a low-melting solid; R_f (EtOAC) 0.67; ν_{max}(Nujol)/cm^{-1} 1715 (C=O); δ(250 MHz; $CDCl_3$) 7.34–7.18 (5 H, m, Ph), 3.10 (1 H, dq, *J* 10.5 and 7, PhC*H*), 2.56 (1 H, dd, *J* 5 and 10.5, CHCO), 1.60 (1 H, d, septet, *J* 4 and 7, CHMe_2), 1.28 (3 H, d, *J* 7, PhCH*Me*), 0.92 (3 H, d, *J* 7, CHMe_AMe$_B$) and 0.90 (3 H, d, *J* 7, CHMe$_A$$Me_B$); *m*/*z* 206 (3%, M$^+$) and 105 (100, PhCHMe) (Found: M$^+$, 206.1302. $C_{13}H_{18}O_2$ requires *M*, 206.1302).

Ethyl 2-*Ethyl*-3-*phenylbut*-3-*enoate* **20**.—Ethyl butanoate (4.0 g, 35 mmol) in THF (10 cm^3) was added dropwise over 5 min to a solution of LDA (40 mmol) in THF (40 cm^3) at −78 °C under nitrogen. After 1 h, acetophenone (4.8 cm^3, 40 mmol) was added dropwise over 5 min, and the solution allowed to warm to 0 °C. The solvent was evaporated under reduced pressure and the residue was diluted with water (30 cm^3) and the mixture extracted with ether (2 × 30 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a pale yellow oil. The oil was dissolved in toluene (100 cm^3) and toluene-*p*-sulfonic acid (0.4 g) was added. The solution was refluxed with a Dean–Stark head for 16 h. The solvent was removed under reduced pressure, the residue diluted with sodium carbonate (3 mol dm^{-3}, 30 cm^3) and the mixture extracted with ether (2 × 30 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed on silica gel (300 g) eluting with light petroleum–diethyl ether (99:1) to give the *ester* (6.77 g, 89%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.47; ν_{max}(film)/cm^{-1} 1715 (C=O) and 1615 (C=C); δ(250 MHz; $CDCl_3$) 7.41–7.24 (5 H, m, Ph), 5.38 (1 H, s, C=CH_AH_B), 5.25 (1 H, s, C=CH$_A$$H_B$), 4.14 (2 H, q, *J* 7, OCH_2Me), 3.41 (1 H, dd, *J* 8.5 and 6.3, C=CCH), 2.10–1.80 (1 H, m, CH_AH_B), 1.80–1.60 (1 H, m, CH$_A$$H_B$), 1.19 (3 H, t, *J* 7, OCH$_2$*Me*) and 0.93 (3 H, t, *J* 7.4, CCH$_2$*Me*) (Found: C, 77.1; H, 8.25. $C_{14}H_{18}O_2$ requires C, 77.1; H, 8.25%).

Ethyl (Z)-2-*Ethyl*-3-*phenylbut*-2-*enoate*.—The ester **20** (2.0 g, mmol) was stirred with sodium ethoxide in ethanol (1 mol dm^{-3}; 20 cm^3) at 20 °C for 16 h. The solvent was evaporated under reduced pressure, the residue was diluted with water (20 cm^3) and the mixture was extracted with ether (2 × 20 cm^3). The extracts were dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (200 g) eluting with light petroleum–diethyl ether (99:1) to give the *ester* (0.95 g, 47%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.53; ν_{max}(film)/cm^{-1} 1710 (C=O); δ(250 MHz; $CDCl_3$) 7.30–7.12 (5 H, m, Ph), 3.83 (2 H, q, *J* 7, OCH_2Me), 2.42 (2 H, q, *J* 7.5, C=CCH_2Me), 2.08 (3 H, s, PhC*Me*), 1.10 (3 H, t, *J* 7.5, C=CCH$_2$*Me*) and 0.81 (3 H, t, *J* 7, OCH$_2$*Me*) (Found: C, 77.1; H, 8.45. $C_{14}H_{18}O_2$ requires C, 77.1; H, 8.25%). Irradiation at the frequency of the signal at δ 2.42 causes an increase in intensity in the signal at δ 2.08, and *vice versa*.

Benzyl (Z)-2-*Ethyl*-3-*phenylbut*-2-*enoate* **21**.—The ester (0.9 g, 4.1 mmol), benzyl alcohol (20 cm^3) and titanium(IV) isopropoxide (2 cm^3) were heated at 120 °C for 7 days. After cooling, the mixture was loaded onto a silica gel column (200 g) and eluted with light petroleum–diethyl ether (99:1) to give the *ester* (1.15 g, 95%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.53; ν_{max}(film)/cm^{-1} 1705 (C=O); δ(250 MHz; $CDCl_3$) 7.35–7.13 (10 H, m, 2 × Ph), 4.83 (2 H, s, CH_2Ph), 2.47 (2 H, q, *J* 7.5, CH_2Me), 2.09 (3 H, s, C=CMe) and 1.10 (3 H, t, *J* 7, CH$_2$*Me*); *m*/*z* 280 (11%, M$^+$) and 91 (100, PhCH$_2$) (Found: M$^+$, 280.1481. $C_{19}H_{20}O_2$ requires *M*, 280.1463). Irradiation at the frequency of the signal at δ 2.47 caused an increase in intensity in the signal at δ 2.09, and *vice versa*.

(2RS,1'SR)-2-(1-*Phenylethyl*)*butanoic Acid* **19a**.—The benzyl ester **21** (200 mg, 0.7 mmol) was stirred in ethyl acetate (10 cm^3) with palladium on carbon (5%; 0.1 g) under hydrogen at room temperature and pressure for 15 min. The catalyst was filtered off and the filtrate evaporated under reduced pressure to give the acid (135 mg, 100%), identical (TLC, IR, ^{1}H NMR) with the acid reported above.

(2RS,3SR)-2-*Isopropyl*-3-*methylbutanedioic Acid* **22**.—The acid **19b** (60 mg, 0.3 mmol) was stirred with ruthenium(IV) oxide (5 mg), sodium periodate (0.2 g, 1 mmol) in water (5 cm^3) and carbon tetrachloride (5 cm^3) at room temperature for 7 days. The solvent was evaporated under reduced pressure and the residue was extracted with ether (8 cm^3). The ether was evaporated under reduced pressure to give the dicarboxylic acid (14 mg, 28%) as a microcrystalline solid, m.p. 176–178 °C (from H_2O) (lit.,[15] 178–180 °C); R_f (EtOAc) 0.09; ν_{max}(Nujol)/cm^{-1} 1715 (C=O); δ(250 MHz; CD_3COCD_3) 3.3 (1 H, dq, *J* 8.5 and 7, MeC*H*), 2.66 (1 H, dd, *J* 8.5 and 5, C*H*CHMe$_2$), 2.0 (1 H, m, C*H*Me$_2$), 1.3 (3 H, d, *J* 7), 0.93 (3 H, d, *J* 7, CHMe_AMe$_B$) and 0.88 (3 H, d, *J* 7, CHMe$_A$$Me_B$) similar to that reported.[15]

(3RS,1'SR)-3-(1-*Phenylethyl*)*pentan*-2-*one* **23a**.—The acid **19a** (85 mg, 0.4 mmol) in THF (5 cm^3) was added to a solution of methyllithium (1.4 mol dm^{-3}; 0.7 cm^3, 1.0 mmol) in THF (5 cm^3) at 0 °C under nitrogen. After 16 h, chlorotrimethylsilane (0.25 cm^3, 2 mmol) was added. After 30 min, the solvent was evaporated under reduced pressure and the residue was diluted with water (10 cm^3) and extracted with ether (2 × 5 cm^3). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The product was chromatographed on silica gel (10 g) eluting with light petroleum–diethyl ether (99:1, v/v) to give the *ketone* (31 mg, 36%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.43; δ(250 MHz; $CDCl_3$) 7.33–7.13 (5 H, m, Ph), 2.90 (1 H,

dq, *J* 10 and 7, PhC*H*), 2.60 (1 H, dt, *J* 4 and 10, CHCO), 2.15 (3 H, s, COMe), 1.46–1.15 (2 H, m, CH_2Me), 1.16 (3 H, d, *J* 7, PhCH*Me*) and 0.70 (3 H, t, *J* 7.5, CH_2Me) coinciding with the signals from the minor component of the reaction described below.

(3RS,1'SR)-4-*Methyl*-3-(1-*phenylethyl*)*pentane*-2-*one* **23b**.—The acid **19b** (25 mg, 0.11 mmol) was similarly treated with methyllithium, except that the mixture was refluxed for 18 h to give the *ketone* (3 mg, 12%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.45; δ(250 MHz; $CDCl_3$) 7.33–7.16 (5 H, m, Ph), 3.11 (1 H, dq, *J* 9 and 7, PhC*H*), 2.74 (1 H, dd, *J* 6.5 and 9, CHCO), 1.96 (3 H, s, COMe), 1.69 (1 H, octet, *J* 7, Me_2CH), 1.18 (3 H, d, *J* 7, PhCH*Me*), 0.92 (3 H, d, *J* 7, $CHMe_AMe_B$) and 0.81 (3 H, d, *J* 7, $CHMe_A\mathit{Me}_B$) coinciding with the signals from the minor component of the reaction described below.

3-(1-*Phenylethyl*)*pentan*-2-*one* **24a**.—The 90:10 mixture of unsaturated ketones **15a** (190 mg, 1 mmol) were stirred with palladium on carbon (5%; 20 mg) in ethyl acetate (10 cm^3) under hydrogen at room temperature and pressure for 2 h. The catalyst was filtered off and the filtrate was evaporated under reduced pressure to give the *ketones* (190 mg, 100%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.43; ν_{max}(film)/cm^{-1} 1710 (C=O); δ(250 MHz; $CDCl_3$) (3*RS*,1'*SR*)(minor): 7.33–7.13 (5 H, m, Ph), 2.90 (1 H, dq, *J* 10 and 7, PhC*H*), 2.60 (1 H, dt, *J* 4 and 10, CHCO), 2.15 (3 H, s, COMe), 1.46–1.15 (2 H, m, CH_2Me), 1.16 (3 H, d, *J* 7, PhCH*Me*) and 0.70 (3 H, t, *J* 7.5, CH_2Me); (3*RS*,1'*RS*)(major): 7.3–7.14 (5 H, m, Ph), 2.94 (1 H, dq, *J* 9.5 and 7, PhC*H*), 2.70–2.61 (1 H, m, CHCO), 1.76 (3 H, s, COMe), 1.75–1.62 (2 H, m, CH_2Me), 1.23 (3 H, d, *J* 7, PhCH*Me*) and 0.85 (3 H, t, *J* 7.4, CH_2Me) in a ratio of 20:80; *m*/*z* 190 (15%, M^+) and 105 (100%, PhCHMe) (Found: M^+, 190.1357. $C_{13}H_{18}O$ requires *M*, 190.1357).

4-*Methyl*-3-(1-*phenylethyl*)*pentan*-2-*one* **24b**.—The unsaturated (3*RS*,1'*SR*) ketone **15b** (200 mg, 1 mmol) was hydrogenated similarly for 4 h to give the *ketones* (200 mg, 100%); R_f (light petroleum–Et_2O, 9:1, v/v) 0.45; ν_{max}(film)/cm^{-1} 1710 (C=O); δ(250 MHz; $CDCl_3$) (3*RS*,1'*SR*)(minor): 7.33:7.16 (5 H, m, Ph), 3.11 (1 H, dq, *J* 7 and 9, PhC*H*), 2.74 (1 H, dd, *J* 6.5 and 9, CHCO), 1.96 (3 H, s, COMe), 1.69 (1 H, octet, *J* 7, Me_2CH), 1.18 (3 H, d, *J* 7, PhCH*Me*), 0.92 (3 H, d, *J* 7, $CHMe_AMe_B$) and 0.81 (3 H, d, *J* 7, $CHMe_A\mathit{Me}_B$); (3*RS*,1'*RS*)(major): 7.28–7.11 (5 H, m, Ph), 3.06 (1 H, dq, *J* 11 and 7, PhC*H*), 2.79 (1 H, dd, *J* 4.5 and 11, COCH), 2.15–2.05 (1 H, m, Me_2CH), 1.66 (3 H, s, COMe), 1.24 (3 H, d, *J* 7, PhCH*Me*) and 1.0 (6 H, d, *J* 7, Me_2CH) in a ratio of 10:90 (Found: C, 82.2; H, 9.6. $C_{14}H_{20}O$ requires C, 82.4; H, 9.8%).

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