Super-acid Catalysed Addition of Allylsilanes to Carbonyl Compounds; Synthetic and Mechanistic Aspects

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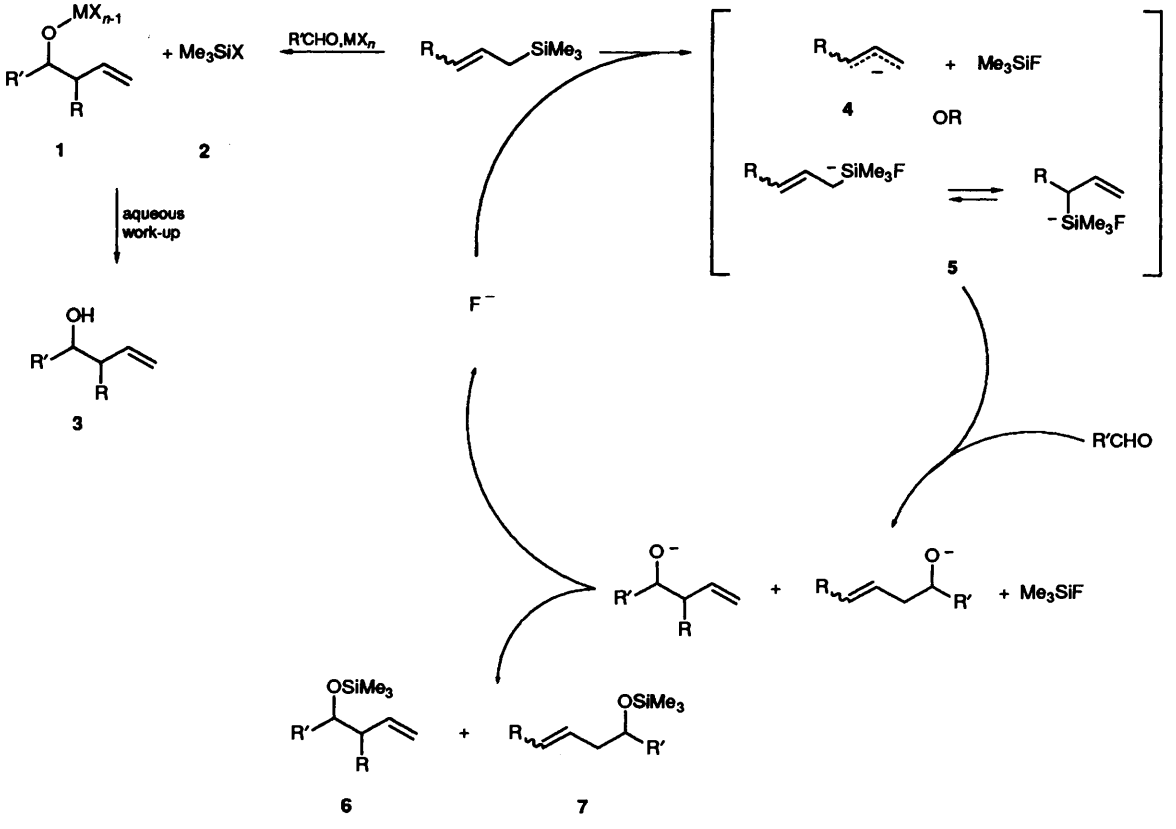
The addition of allyltrimethylsilane **8** to a variety of aldehydes and one ketone (cyclohexanone) was found to be induced by the super-acid $TfOH_2^+B(OTf)_4^-$ (Tf ≡ CF_3SO_2). In contrast to the analogous Lewis acid catalysed reaction, only catalytic amounts (0.5–3 mol%) of the super-acid were required. Modest stereoselectivities were observed with the 'α-chiral' aldehydes **15**, **21** and **24**; in the last two cases, the sense of the selectivity was the opposite of that predicted by 'chelation control'. Application of the method to the addition of but-2-enyltrimethylsilane **29** to benzaldehyde demonstrated that, unlike the fluoride-catalysed analogue, it is regioselective with respect to allylic inversion. Control experiments employing Me_3SiOTf, $B(OTf)_3$ or TfOH as catalysts established that none is sufficiently active to account for the results. Two possible mechanisms are postulated, one in which the activating species is a superacidic proton and one in which it is an 'Me_3Si^+' unit. On the basis of the stereochemical results, it is argued that the latter is marginally more likely.

The addition of allylsilanes to aldehydes and ketones[1]† has been quite intensively researched since the original reports in the mid-1970s.[3] Aside from rare examples involving unusually reactive substrates,[3a] the reaction does not occur spontaneously but requires a catalyst or promoter. As illustrated in Scheme 1, the conditions generally involve either (i) a strong Lewis acid, or (ii) a source of fluoride ions. Although both types of reaction give good yields and have been widely used, they do have certain disadvantages. In the former case, the Lewis acids commonly used (*e.g.* $TiCl_4$, $SnCl_4$, $BF_3{\cdot}OEt_2$, $AlCl_3$),[1b] are all based on strongly oxophilic metal ions. Procedures involving these reagents always seem to require stoichiometric or near-stoichiometric quantities of the Lewis

† In our earlier report[2] we referred to this as 'the Sakurai reaction'. We have since realised that this term is more appropriate for the conjugate addition of allylsilanes to α,β-unsaturated ketones. See, *e.g.*, ref. 1*b*.



Scheme 1

Table 1 Synthesis of homoallyl alcohols **11** as shown in Scheme 2

Aldehyde	R	Desilylation method[a]	Yield of **11** (%)
9a	Bu	A	60[b]
9b	$PhCH_2CH_2$	B	76
9c	Pr^i	A	77[b]
9d	$c\text{-}C_6H_{11}$	B	81
9e	Bu^t	C	86
9f	Ph	B	95
9g	$p\text{-}MeOCOC_6H_4$	B	85[c]
9h	$p\text{-}O_2NC_6H_4$	B	95
9i	$p\text{-}ClC_6H_4$	B	60

[a] A, HCl aq., Et_2O; B, HCl aq., MeOH, CH_2Cl_2; C, HCl aq., MeOH, Et_2O. For further details, see Experimental section. [b] Purified by distillation. [c] Purified by flash chromatography.

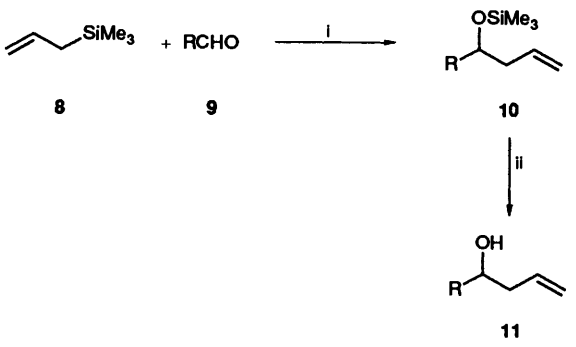
acid,* presumably because of the inability of species **1** and **2** formed in the addition (Scheme 1) to react together efficiently giving silyl homoallyl ethers **6** and regenerated Lewis acid. This constraint is at best inconvenient, and could lead to more serious problems such as side reactions or difficulties in the isolation of the final products, homoallyl alcohols **3**.

In contrast the reactions promoted by fluoride ions are catalytic, presumably *via* the cycle depicted in Scheme 1.[7] However, in these cases the reaction intermediates **4** or **5**[8] do not retain a 'regiochemical memory' of the starting allylsilane, so that the product silyl homoallyl ethers are often formed as mixtures of isomers **6** and **7**.

Recently we reported a new variant on the addition of allylsilanes to aldehydes and ketones,[2] in which the reaction was promoted by catalytic quantities (*ca.* 0.5 mol%) of the superacid trifluoromethanesulfoxonium tetrakis(trifluoromethanesulfonyl)boronate ($TfOH_2^+B(OTf)_4^-$; $Tf \equiv CF_3SO_2$),[9] readily prepared from BBr_3 and TfOH. This method combined the advantages of those previously discussed, in that it was both catalytic and regiospecific with respect to allylic inversion. It was also of mechanistic interest, if only because it demonstrated the ability of a reagent which would normally be considered highly aggressive[10] to mediate a reaction involving rather sensitive starting materials and products. The purpose of this paper is (*a*) to provide full details of the work described in our previous report, (*b*) to describe additional experiments which further delineate the scope of the reaction, with special reference to stereoselectivity, and (*c*) to discuss results relating to the mechanism of the reaction. In particular, we present arguments which suggest that the mechanism proposed in the earlier report ('H^+ catalysis') may be incorrect, and that an alternative ('Me_3Si^+ catalysis') may be more probable.

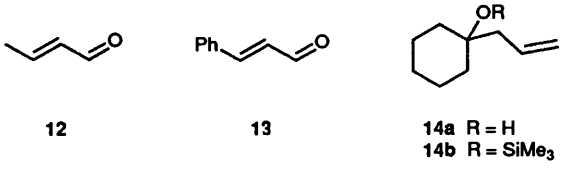
Results and Discussion

Scheme 2 and Table 1 summarise the application of our method to the synthesis of a number of homoallylic alcohols **11** from allyltrimethylsilane **8** and simple, achiral aldehydes **9**. In most cases (the exception being aldehyde **9g**) the procedure gave a crude product which was pure by TLC and NMR. The relatively volatile products from **9a** and **9c** were purified by distillation to free them from solvent. The fact that the yields are not quantitative can probably be ascribed, at least in part, to losses on work-up and evaporation of solvent; most of the reactions were carried out on a 1 mmol scale. Where the additions could be monitored by TLC, they were usually complete within 3 min and, with one exception, always within 20 min. The exception was the reaction of *p*-chlorobenzaldehyde **9i** which, surprisingly, took 72 h to go to completion.



Scheme 2 *Reagents and conditions:* i, CH_2Cl_2, room temp., $TfOH_2^+B(OTf)_4^-$ (0.5 mol%); ii, H^+, H_2O

A survey of Table 1 indicates that the addition is not especially sensitive to steric hindrance, is effective with both aliphatic and aromatic aldehydes, and in the latter case is tolerant of nitro and ester substituents. The method could not, however, be applied to the α,β-unsaturated aldehydes but-2-enal **12** and 3-phenylprop-2-enal **13**. In both cases the reaction



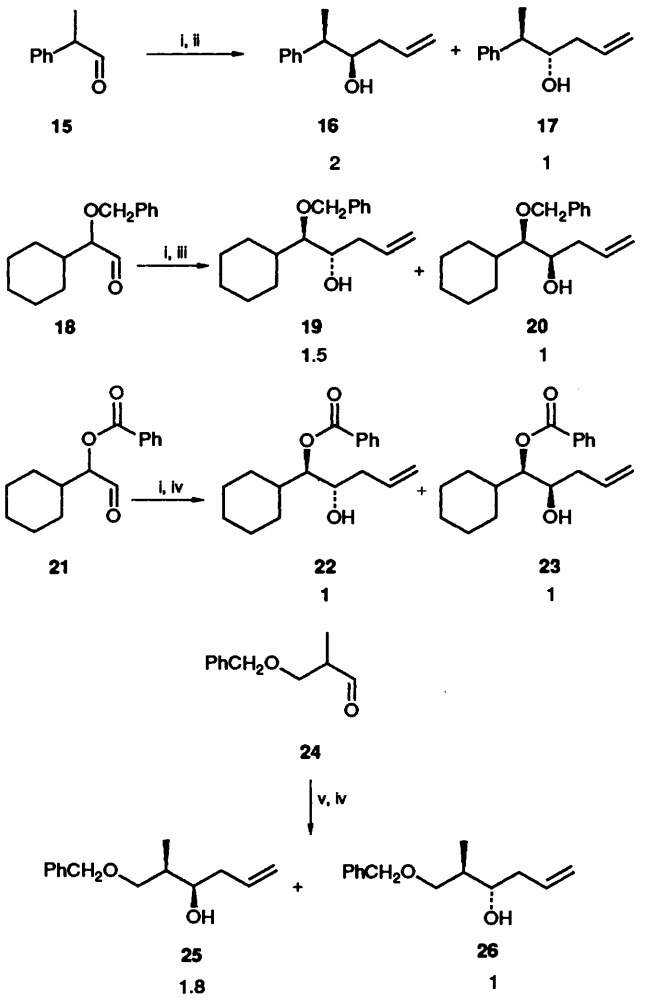
12 **13** **14a** R = H; **14b** R = $SiMe_3$

was incomplete and gave a complex mixture of products. The procedure was attempted with one ketonic substrate, cyclohexanone. In this case the addition was unsatisfactory under the standard conditions, giving a low yield of the alcohol **14a** accompanied by non-polar side-products which may have resulted from the elimination of water. However, the reaction could be performed successfully under a different set of conditions employing a lower temperature [−40 °C, 90 min, 3 mol% of $TfOH_2^+B(OTf)_4^-$], giving the alcohol **14a** in 80% yield. It was not necessary to desilylate the intermediate silyl ether **14b** by treatment with acid; quenching the reaction mixture with aqueous sodium hydrogen carbonate gave the alcohol **14a** directly.

We also explored a number of variations on the procedure in Scheme 2. It transpired that it was necessary to add the superacid catalyst to a solution containing both the carbonyl compound and the allylsilane. The other possible orders of addition gave unsatisfactory results. When alternative solvents were explored, it was found that toluene gave similar results to dichloromethane, acetonitrile allowed the reaction to proceed at a much reduced rate, and ether was unsuitable (resulting in destruction of the aldehyde but giving no identified products). Finally, if the second step in Scheme 2 was omitted it proved possible to isolate the initial adducts **10** by flash chromatography. This procedure was tested on the aldehydes **9d** and **9f**, giving products **10d** and **10f** in yields of 79 and 60% respectively.

The allylation was also applied to a number of substrates containing chiral centres. The results are summarised in Scheme 3. Unfortunately, none of the stereoselectivities was sufficiently pronounced to be of practical value, although the result with

* See the remarks on p. 16 of ref. 1*a*, and also in ref. 4. Denmark *et al.* have demonstrated that an intramolecular analogue of the addition can take place with sub-stoichiometric amounts of Lewis acids, but the quantities involved were not such as to imply especially efficient turnover (0.25 equiv. of $SnCl_4$, 0.55 equiv. of $BF_3{\cdot}OEt_2$).[5] We are only aware of one intermolecular example in which turnover has been observed, the addition of allyltrimethylsilane to benzaldehyde catalysed by Ph_2BOTf.[6] In the light of our own work,[2] it is possible that the Lewis acid was not in fact the true catalyst.

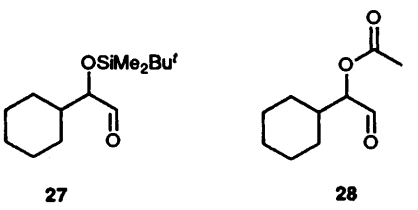


Scheme 3 *Reagents and conditions:* i, **8** (2 equiv.), CH_2Cl_2, $TfOH_2^+$-$B(OTf)_4^-$ (0.5–2 mol%), room temp.; ii, HCl aq., MeOH, Et_2O; iii, HCl aq., MeOH; iv, $NaHCO_3$ aq.; v, **8** (2 equiv.), CH_2Cl_2, $TfOH_2^+$ $B(OTf)_4^-$ (2.5 mol%), −40 °C (product ratios beneath each compound)

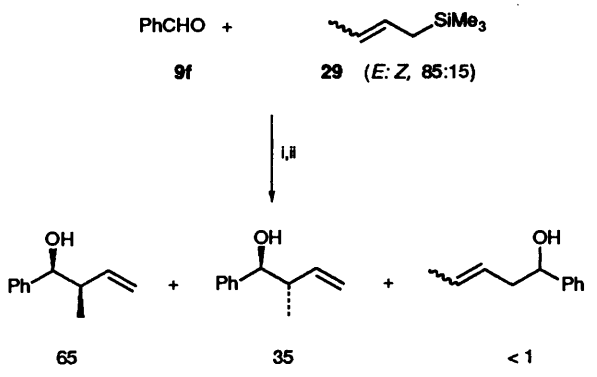
unfunctionalised aldehyde **15**, which is consistent with Cram's rule, is quite respectable in the context of the analogous Lewis acid catalysed reactions. Thus, the present reaction was conducted at room temperature, while use of $TiCl_4$, $BF_3{\cdot}OEt_2$ or $SnCl_4$ at −78 °C is reported to give similar selectivity.[11] In the present case the proportion of the 'Cram product' **16** could be increased by lowering the temperature, ratios of *ca.* 4:1 being obtained at −40 °C.*

Although they show modest selectivities (if any) the reactions with *O*-substituted substrates **18**, **21** and **24** do at least demonstrate that benzyloxy and benzoyloxy substituents are compatible with the conditions. The allylation of compound **21** did, however, take 24 h to reach completion, implying that the α-benzoyloxy group has a substantial decelerating effect. The method could not be applied successfully to substrates **27** and **28**, probably because of desilylation in the former case and acetyl migration in the latter. It may be noted that the sense of the stereoselectivities observed for compounds **18** and **24** is contrary to that which is predicted by chelation control,[12] and which had previously been observed for allylations of the same substrates employing allyltributylstannane–$TiCl_4$[13] and allyltrimethylsilane–$SnCl_4$[11] respectively.

* Reactions at lower temperatures were unsuccessful, probably because the super-acid failed to dissolve in the reaction mixture.



The regioselectivity of the method with respect to allyl inversion (*cf.* Scheme 1) was tested by treatment of benzaldehyde **9f** with crotyltrimethylsilane **29**. As shown in Scheme 4,



Scheme 4 *Reagents and conditions:* i, CH_2Cl_2, room temp., $TfOH_2^+$-$B(OTf)_4^-$ (0.5 mol%); ii, $NaHCO_3$ aq. (product ratios given beneath each compound)

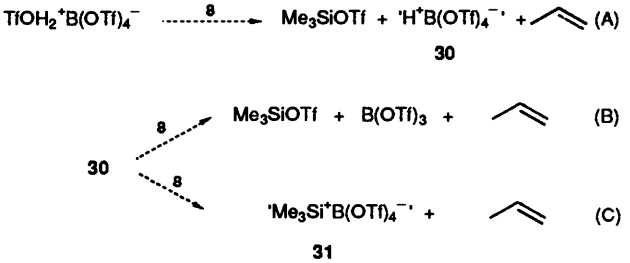
attack of the aldehyde occurred almost exclusively at the γ-carbon of the silane. The stereochemical course of the reaction cannot be precisely defined at this stage because of the fact that only one isomeric composition of **29** was employed, but it clearly differs significantly from the $TiCl_4$-induced addition of **29** to aliphatic aldehydes in which the *E*-silane is strongly *syn*-selective and the *Z*-silane moderately so.[14]

Mechanistic Considerations.—It is well established that allylsilanes may be protodesilylated by Brønsted acids as illustrated in Scheme 5. For example it has been reported that Me_3SiOTf

Scheme 5

may be prepared by treatment of compound **8** with TfOH in CH_2Cl_2 for 1 h at room temperature,[15] and NMR experiments in our laboratory (with $CDCl_3$ as solvent) have suggested that the reaction is essentially complete within 5 min. Thus, it seemed very likely that the allylsilane and super-acid would interact in some way, and that the 'true catalyst' would be a product thereof.

Possible modes of reaction between compound **8** and $TfOH_2^+B(OTf)_4^-$, are shown in Scheme 6. Of the potential catalysts represented in this Scheme we were able to show that

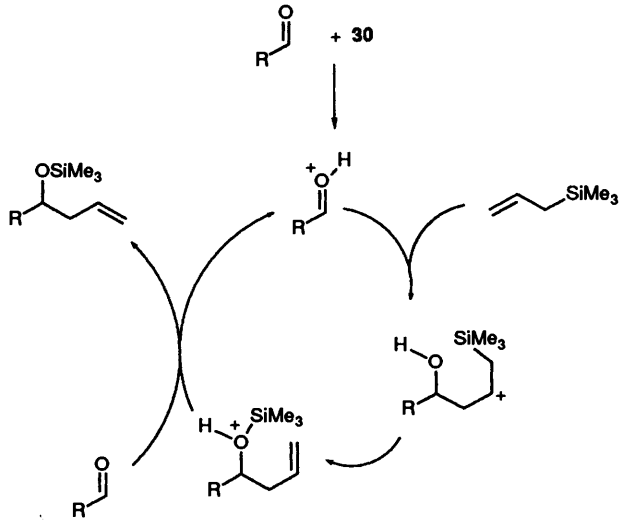


Scheme 6

neither Me_3SiOTf nor $B(OTf)_3$ is responsible for the super-acid catalysed addition. Control experiments showed that, although both did catalyse the allylation, they were less active than the super-acid by several orders of magnitude. TfOH was shown to be a similarly poor catalyst, almost certainly because it reacted with compound **8** to generate Me_3SiOTf *in situ*.

Further clarification was provided by NMR studies of the reaction between $TfOH_2{}^+B(OTf)_4{}^-$ and compound **8**. An ^{11}B NMR experiment performed in $CDCl_3$ was especially informative, as it showed that the sharp singlet due to $B(OTf)_4{}^-$ (δ −3.21, relative to $BF_3{\cdot}OEt_2$ external standard) was unaffected by addition of a substantial excess of compound **8**. The result suggests quite strongly that reaction mode B in Scheme 6 is unimportant. ^1H and ^{13}C NMR experiments were more difficult to interpret. Although they confirmed that a clean and rapid reaction took place between $TfOH_2{}^+B(OTf)_4{}^-$ and the first equivalent of compound **8** (presumably reaction A in Scheme 6), the addition of further allylsilane seemed to have more complex consequences* (it may be noted that the resulting solutions were ineffective as catalysts, implying that the actual catalytic species is either not generated or is not stable in the presence of compound **8** and absence of aldehyde).

In the light of the above experiments, there seemed to be two reasonable mechanistic hypotheses. The first ('H^+ catalysis') is shown in Scheme 7. It is supposed that, of the

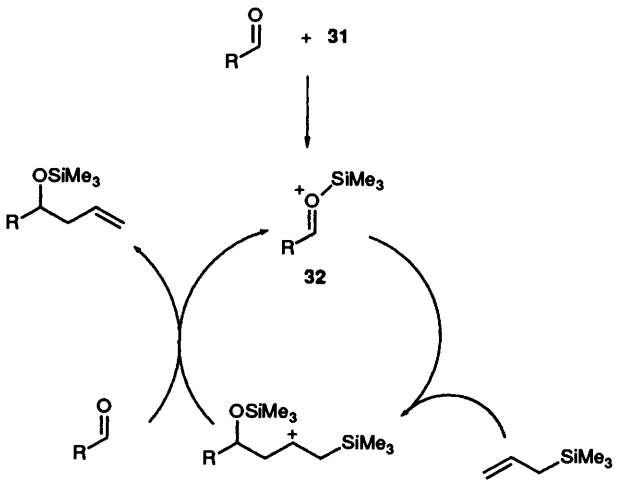


Scheme 7 Counterion for all cations = $B(OTf)_4{}^-$

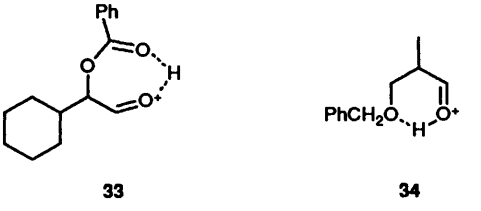
processes in Scheme 6, only reaction A takes place, and the resulting species **30** (the 'true catalyst') acts by protonation of the aldehyde. It should be emphasized that compund **30** may only have a notional existence; in the presence of the aldehyde, the proton need never be directly attached to the $B(OTf)_4{}^-$ anion.

The second possibility ('Me_3Si^+ catalysis') is shown in Scheme 8. In this case both processes A and C take place and the resulting 'super-silylating agent' **31** initiates the reaction by silylation of the aldehyde. Again, it is not necessarily implied that compound **31** has a real existence, as the intermediate **32** could be formed without its intervention (however, see below).

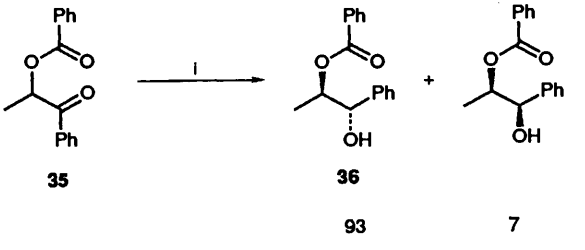
Although we suggested the 'H^+ catalysis' mechanism in our



Scheme 8 Counterion for all cations = $B(OTf)_4{}^-$



preliminary communication,[2] we are now inclined to suspect that 'Me_3Si^+ catalysis' is more likely. A major reason is the stereochemical results obtained with the oxygenated aldehydes **21** and **24** (Scheme 3). If 'H^+ catalysis' were operative, we feel that in both these cases it is likely that protonation of the substrate should give species with intramolecular hydrogen bonds (*e.g.* **33** and **34**), and that these should react to give predominantly the 'chelation-controlled' products **23** and **26** respectively. In the case of the benzoyloxy aldehyde **21**, these speculations are given some substance by the work of Fujita and Hiyama on acid-catalysed silane reductions. As shown in Scheme 9, the reduction of the benzoyloxy ketone **35** with



Scheme 9 *Reagents and conditions:* i, Et_3SiH, CF_3CO_2H (product ratio beneath compounds)

triethylsilane in trifluoroacetic acid was found to give the 'chelation-controlled' product **36** with quite respectable diastereoselectivity[16] (the benzyl-protected analogue, which may be compared with compound **18**, did not however give a stereoselective reaction). Although there is, as far as we are aware, no such precedent relating to the β-benzyloxy aldehyde **24**, we found that semi-empirical molecular orbital calculations using the AM1 method (as implemented in AMPAC, supplied as part of the QUANTA package by Polygen Ltd. and running on a Silicon Graphics IRIS 4D25TG workstation) predicted that the most stable configuration after protonation should indeed be the species **34**.

Additional support (of a circumstantial nature) for the mechanism shown in Scheme 8 comes from our work on the

* In an early experiment, a ^1H NMR spectrum taken after addition of a second equivalent of compound **8** to $TfOH_2{}^+B(OTf)_4{}^-$ was interpreted as indicating that some of the allylsilane survived, implying that processess B and/or C are slow and promoting the notion of 'H^+ catalysis' (*vide infra*), as suggested in our preliminary communication.[2] However, later attempts failed to support this interpretation and we must now regard these experiments as inconclusive.

catalysis of the allylation reaction by silylating agents. Thus, as described separately,[17] we followed up the discovery that Me_3SiOTf was a rather poor catalyst (*vide supra*)* by finding (i) that Me_3SiI is significantly more effective, and (ii) that the 'super-silylating' agent **31** does in fact have a real existence [being generated in CH_2Cl_2 or $CDCl_2$ from the interaction of $B(OTf)_3$ and Me_3SiOTf] and is of comparable effectiveness as a catalyst to the super-acid itself. Moreover, use of Me_3SiI as catalyst for the reaction between compounds **24** and **8** gave alcohols **25** and **26** in the ratio 1.4:1, which may be compared with the ratio of 1.8:1 obtained with the super-acid (Scheme 3). While these results may of course have no bearing on the super-acid catalysed reaction, they undoubtedly enhance the plausibility of the mechanism in Scheme 8.

Experimental

^1H NMR spectra were recorded on Bruker MSL 300 (300 MHz), Bruker WP 80 (80 MHz) or JEOL JNM PMX 60 (60 MHz) instruments. ^{13}C NMR spectra were recorded on the MSL 300 (75.5 MHz). Unless otherwise stated, all spectra were recorded using $CDCl_3$ as solvent, with tetramethylsilane as the internal standard. *J*-Values are given in Hz. IR spectra were recorded on a Perkin-Elmer 883 IR spectrophotometer. Microanalyses were carried out by University College Dublin microanalytical laboratory. Dichloromethane was distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodiobenzophenone. Aldehydes and ketones used were purified by distillation or other methods as indicated. All reactions were carried out under an atmosphere of argon. $TfOH_2{}^+B(OTf)_4{}^-$ was prepared after the method of Olah *et al.*[9b] 'Work-up' refers to the addition of saturated aqueous $NaHCO_3$, extraction with CH_2Cl_2 or Et_2O (as specified), drying of the extract (Na_2SO_4) and evaporation of the solvent.

Oct-1-en-4-ol **11a**.—To a solution of pentanal **9a** (430 mg, 5 mmol, 530 mm^3) and allyltrimethylsilane **8** (1.14 g, 10 mmol, 1.60 cm^3) in CH_2Cl_2 (10 cm^3) was added $TfOH_2{}^+B(OTf)_4{}^-$ (20 mm^3, 1 mol%). After 20 min, Et_2O (10 cm^3) and hydrochloric acid (36%, 1 cm^3) were added. After 0.5 h work-up and fractional distillation of the solvent and residue gave the alkenol **11a** as a colourless liquid (378 mg, 59%); b.p. (bath temp) 90 °C/12 mmHg (lit.,[18] b.p. 62 °C/7 mmHg); δ_H(60 MHz) 1.40–1.60 (10 H, m, C_4H_9 + OH), 1.90–2.27 (2 H, m, $CH_2CH{=}CH_2$), 3.30–3.70 (1 H, m, OCH), 4.63–5.10 (2 H, m, $CH{=}CH_2$) and 5.37–6.00 (1 H, m, $CH{=}CH_2$).

1-Phenylhex-5-en-3-ol **11b**.—To a solution of 3-phenylpropanal **9b** (134 mg, 1 mmol, 131 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2{}^+B(OTf)_4{}^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 3 min.* The solvent was evaporated and Et_2O (5 cm^3), methanol (1 cm^3) and hydrochloric acid (36%, 8 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 1.5 h.† Work-up (Et_2O) gave the alkenol **11b** as a colourless liquid, pure by TLC (133 mg, 76%); δ_H(80 MHz) 1.60–2.30 (5 H, m, $PhCH_2CH_2$ + OH), 2.53–2.85 (2 H, m, $OCHCH_2CH{=}CH_2$), 3.50–3.80 (1 H, m, OCH), 4.93–5.20 (2 H, m, $CH{=}CH_2$), 5.55–6.08 (1 H, m, $CH{=}CH_2$) and 7.20 (5 H, Ph) [lit.,[19] δ_H(90 MHz) 1.60–1.92 (2 H, m), 2.10–2.40 (2 H + OH, m), 2.50–2.90 (2 H, m), 3.42–3.70 (1 H, m), 4.95–5.20 (2 H, m), 5.55–6.05 (1 H, m) and 7.15 (5 H, m)].

2-Methylhex-5-en-3-ol **11c**.—To a solution of 2-methylpropanal **9c** (360 mg, 5 mmol, 454 mm^3) and allyltrimethylsilane **8** (1.14 g, 10 mmol, 1.60 cm^3) in CH_2Cl_2 (10 cm^3) was added $TfOH_2{}^+B(OTf)_4{}^-$ (10 mm^3, 0.5 mol%). After 25 min Et_2O (10 cm^3) and hydrochloric acid (36%, 0.5 cm^3) were added. After 20 min work-up and fractional distillation of the solvent and residue gave the alkenol **11c** as a colourless liquid (438 mg, 77%); b.p. (bath temp.) 90 °C/12 mmHg; δ_H(60 MHz) 0.66–1.10 (6 H, m, Me), 1.33–1.90 (1 H, m, Me_2CH), 1.90–2.40 (3 H, m, $CH_2CH{=}CH_2$ + OH), 3.20–3.60 (1 H, m, OCH), 4.80–5.20 (2 H, m, $CH{=}CH_2$), 5.50–6.20 (1 H, m, $CH{=}CH_2$) [lit.,[20] δ_H 0.7 (6 H, d), 1.2–2.4 (3 H + OH, m), 3.2–3.8 (1 H, m), 4.9–5.5 (2 H, m) and 5.6–6.5 (1 H, m)].

1-Cyclohexylbut-3-enol **11d**.—To a solution of cyclohexanecarbaldehyde **9d** (139 mg, 1 mmol, 150 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (5 cm^3) was added $TfOH_2{}^+B(OTf)_4{}^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 20 min. Methanol (1 cm^3) and hydrochloric acid (36%, 5 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 1.5 h. Work-up (CH_2Cl_2) gave the alkenol **11d** as a colourless liquid (125 mg, 81%); δ_H(80 MHz) 0.75–2.00 (11 H, m, c-Hex), 2.10–2.34 (3 H, m, CH_2 + OH), 3.35–3.50 (1 H, m, OCH), 4.95–5.25 (2 H, m, $CH{=}CH_2$), 5.60–6.13 (1 H, m, $CH{=}CH_2$) [lit.,[21] δ_H(CCl_4) 0.80–2.10 (12 H, m), 2.10–2.40 (2 H, m), 3.10–3.50 (1 H, m) and 4.80–6.10 (3 H, m)].

1-Cyclohexyl-1-(trimethylsilyloxy)but-3-ene **10d**.—To a solution of cyclohexanecarbaldehyde **9d** (139 mg, 1 mmol, 150 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (5 cm^3) was added $TfOH_2{}^+B(OTf)_4{}^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 20 min. Evaporation of solvent and purification by flash chromatography (hexane–Et_2O, 5:3) gave the title compound **10d** as a colourless liquid (222 mg, 79%); δ_H(80 MHz, ref. $CHCl_3$ = 7.26 ppm) 0.09 (9 H, s, Me_3Si), 0.80–2.10 (11 H, m, c-Hex), 2.10–2.40 (2 H, m, CH_2), 3.30–3.60 (1 H, dd, *J* 5, 6, OC*H*), 4.85–5.25 (2 H, m, $CH{=}CH_2$) and 5.55–6.15 (1 H, m, $CH{=}CH_2$).

Desilylation to compound **11d** was achieved by addition of methanol (1 cm^3) and hydrochloric acid (36%, 12 drops) to a solution of compound **10d** (222 mg, 1.6 mmol) in CH_2Cl_2 (4 cm^3). Analysis by TLC (hexane–Et_2O, 5:3) indicated the conversion to be complete in 40 min and work-up (CH_2Cl_2) gave compound **11d** (140 mg, 57%), pure by TLC and NMR.

2,2-Dimethylhex-5-en-3-ol **11e**.—To a solution of 2,2-dimethylpropanal **9e** (86 mg, 1 mmol, 108 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2{}^+B(OTf)_4{}^-$ (2 mm^3, 0.5 mol%). After 15 min the solvent was evaporated and Et_2O (5 cm^3), methanol (1 cm^3) and hydrochloric acid (36%, 5 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 5 min. Work-up (Et_2O) gave the alkenol **11e** as a colourless liquid (110 mg, 86%); δ_H(80 MHz) 0.92 (9 H, s, Me), 1.80 (br s, OH), 2.00–2.55 (2 H, m, CH_2), 3.18–3.35 (1 H, dd, *J* 3, 11, OCH), 4.95–5.25 (2 H, m, $CH{=}CH_2$) and 5.64–6.15 (1 H, m, $CH{=}CH_2$) [lit.,[20] δ_H 0.9 (9 H, s), 1.7–2.4 (2 H + OH, m), 3.2 (1 H, m), 4.8–5.2 (2 H, m) and 5.4–6.2 (1 H, m)].

* The fact that Me_3SiOTf is capable of catalysing the allylation at all was itself of interest, as previous reports had suggested that it would be completely ineffective.[17]

† TLC analysis of the reaction mixtures for the superacid-catalysed additions generally showed two product spots. One, which was slower-running than the aldehyde starting material, corresponded to the alcohol **11** while the other, which was fast-running, corresponded to the silylated product **10**. The latter disappeared during the second stage of the procedure (where applicable).

1-*Phenylbut*-3-*enol* **11f**.—To a solution of benzaldehyde **9f** (106 mg, 1 mmol, 100 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+$-$B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in less than 3 min. Methanol (1 cm^3) and hydrochloric acid (36%, 5 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 45 min. Work-up (CH_2Cl_2) gave compound **11f** as a colourless liquid, pure by TLC (140 mg, 95%); δ_H(80 MHz) 2.44 (2 H, t, *J* 7, CH_2), 2.54 (br s, OH), 4.63 (1 H, t, *J* 7, OCH), 4.90–5.20 (2 H, m, CH=CH_2), 5.50–6.00 (1 H, m, C*H*=CH_2) and 7.28 (5 H, s, Ph) [lit.,[20] δ_H 2.1 (OH, d), 2.3–2.6 (2 H, m), 4.6–5.0 (2 H, m), 5.5–6.4 (1 H, m) and 7.5 (5 H, s)].

1-*Phenyl*-1-(*trimethylsilyloxy*)*but*-3-*ene* **10f**.—To a solution of benzaldehyde (106 mg, 1 mmol, 100 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in less than 3 min. Evaporation of solvent and purification by flash chromatography (hexane) gave compound **10f** as a colourless liquid (132 mg, 60%); δ_H(80 MHz) 0.09 (9 H, s, Me_3Si), 2.49 (2 H, t, *J* 7, CH_2), 4.79 (1 H, t, *J* 7, OCH), 4.87–5.29 (2 H, m, CH=CH_2), 5.54–6.14 (1 H, m, C*H*=CH_2) and 7.34 (5 H, s, Ph).

Desilylation to compound **11f** was achieved by the addition of methanol (1 cm^3) and hydrochloric acid (36%, 5 drops) to a solution of compound **10f** (132 mg, 0.6 mmol) in CH_2Cl_2 (4 cm^3). Analysis by TLC (hexane–Et_2O, 5:3) indicated the conversion to be complete in 1 h. Work-up (CH_2Cl_2) gave compound **11f** (61 mg, 67%), pure by TLC and NMR.

Methyl 4-(1-*Hydroxybut*-3-*enyl*)*benzoate* **11g**.—To a solution of methyl 4-formylbenzoate **9g** (164 mg, 1 mmol) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 10 min. Methanol (1 cm^3) and hydrochloric acid (36%, 5 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 10 min. Work-up followed by flash chromatography (hexane–Et_2O, 1:1) gave **11g** as a colourless liquid, pure by TLC (174 mg, 85%); δ_H (60 MHz) 2.43 (2 H, t, *J* 7, OCHCH_2), 3.07 (br s, OH), 3.90 (3 H, s, Me), 4.73 (1 H, t, *J* 7, OCH), 4.90–5.30 (2 H, m, CH=CH_2), 5.40–6.15 (1 H, m, C*H*=CH_2), 7.20–7.46 (2 H, m, Ph) and 7.86–8.10 (2 H, m, Ph) [lit.,[22] δ_H 2.3 (2 H, t, *J* 6), 3.25 (br s, OH), 3.80 (3 H, s), 4.6 (1 H, t, *J* 6), 4.80–5.10 (2 H, m), 5.30–5.90 (1 H, m), 7.2 (2 H, d) and 7.8 (2 H, d)].

1-(4-*Nitrophenyl*)*but*-3-*enol* **11h**.—To a solution of 4-nitrobenzaldehyde **9h** (151 mg, 1 mmol) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 3 min. Methanol (1 cm^3) and hydrochloric acid (36%, 5 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 30 min. Work-up (CH_2Cl_2) gave compound **11h** as a colourless liquid, pure by TLC (183 mg, 95%); δ_H(60 MHz) 2.46 (2 H, t, *J* 8, OCHCH_2), 2.80 (br s, OH), 4.77 (1 H, t, *J* 8, OCH), 4.87–5.23 (2 H, m, CH=CH_2), 5.36–6.10 (1 H, m, CH=CH_2), 7.30–7.46 (2 H, m, Ph) and 7.93–8.10 (2 H, m, Ph) [lit.,[23] δ_H(CCl_4) 2.40 (2 H, t, *J* 7), 2.77 (br s, OH), 4.70 (1 H, t, *J* 7), 4.70–6.00 (3 H, m), 7.33 (2 H, d, *J* 9) and 7.95 (2 H, d, *J* 9)].

1-(4-*Chlorophenyl*)*but*-3-*enol* **11i**.—To a solution of 4-chlorobenzaldehyde **9i** (recrystallised from methanol–water, 3:1) (141 mg, 1 mmol) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 72 h. Methanol (1 cm^3) and hydrochloric acid (36%; 5 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 30 min. Work-up (CH_2Cl_2) gave the title compound **11i** as a colourless liquid, pure by TLC (107 mg, 60%); δ_H(60 MHz) 2.43 (2 H + OH, t, *J* 6, OCHCH_2), 4.60 (1 H, t, *J* 6, OCH), 4.80–5.23 (2 H, m, CH=CH_2), 5.33–6.13 (1 H, m, CH=CH_2) and 7.20 (4 H, s, Ph) [lit.,[23] δ_H(CCl_4) 2.30 (2 H, t, *J* 7), 2.95 (br s, OH), 4.50 (1 H, t, *J* 7), 4.75–6.00 (3 H, m) and 7.10 (4 H, s)].

1-*Allylcyclohexanol* **14a**.—To a solution of cyclohexanone (98 mg, 1 mmol, 104 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) at −40 °C was added $TfOH_2^+B(OTf)_4^-$ (12 mm^3, 3 mol%). After 1.5 h at −40 °C the mixture was quenched (saturated aqueous $NaHCO_3$), warmed to room temperature and the organic phase was separated, dried (Na_2SO_4), and evaporated. Purification of the residue by flash chromatography (hexane–Et_2O, 3:2) yielded the title compound **14a** as a colourless liquid, pure by TLC (114 mg, 81%); δ_H(80 MHz) 1.50 (11 H, s, c-Hex + OH), 2.23 (2 H, d, *J* 7, HOCCH_2), 4.93–5.23 (2 H, m, CH=CH_2) and 5.65–6.15 (1 H, m, C*H*=CH_2) [lit.,[24] δ_H(60 MHz, CCl_4) 1.47 (10 H, s), 2.16 (2 H, dt, *J* 7, 1), 2.25 (br s, OH), 5.00 (2 H, m) and 5.83 (1 H, m)].

syn(l)- *and* anti(u)-2-*Phenylhex*-5-*en*-3-*ol* **16** *and* **17**.—To a solution of purified[11] 2-phenylpropanal **15** (134 mg, 1 mmol, 133 mm^3) and allyltrimethylsilane **8** (228 mg, 2 mmol, 320 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 3 min. The solvent was evaporated and Et_2O (5 cm^3), methanol (1 cm^3) and hydrochloric acid (36%, 10 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 0.5 h. Work-up (Et_2O) and purification by flash chromatography (hexane–Et_2O, 3:2) gave a mixture of compounds **16** and **17** as a colourless liquid pure by TLC and NMR 120 mg, 69%, ratio 2:1 by ^1H NMR); δ_H(300 MHz) 1.28 (*u*), 1.33 (*l*) (3 H, d, *J* 7, Me), 1.75 (br s, OH), 1.90–2.30 (2 H, m, OCHCH_2), 2.75 (1 H, q, *J* 7, MeC*H*), 3.65–3.80 (1 H, m, OC*H*), 4.95–5.20 (2 H, m, CH=CH_2), 5.75–6.00 (1 H, m, C*H*=CH_2) and 7.15–7.35 (5 H, m, Ph) [lit.,[25] δ_H(CCl_4) 1.27 (*u*), 1.29 (*l*) (3 H, d, *J* 7), 1.72 (br s, OH), 2.00 (2 H, m), 2.65 (1 H, q), 3.60 (1 H, m), 4.86–5.06 (2 H, m), 5.90–6.52 (1 H, m) and 7.16 (5 H, m)].

anti(u)- *and* syn(l)-1-*Cyclohexyl*-1-*benzyloxypent*-4-*en*-2-*ol* **19** *and* **20**.—To a solution of 1-cyclohexylprop-2-en-1-ol[26,27] (420 mg, 3 mmol) in THF (8 cm^3) was added NaH (80% disp. in oil; 130 mg, 4.5 mmol, washed in hexane) at 0 °C. After 0.5 h tetrabutylammonium iodide[28] (11 mg, 1 mol%) and benzyl bromide (530 mg, 3.1 mmol, 370 mm^3) were added. After 1 day Celite (0.2 g) was added and the solvent evaporated. Elution with pentane and evaporation of solvent yielded 3-benzyloxy-3-cyclohexylprop-1-ene[13] as a colourless liquid pure by TLC (672 mg, 97%); δ_H(60 MHz) 1.00–1.90 (11 H, m, c-Hex), 3.20–3.60 (1 H, m, OCH), 4.14–4.70 (2 H, m, CH_2Ph), 4.85–6.10 (3 H, m, CH=CH_2) and 7.23 (5 H, s, Ph).

Through a solution of this material (1.26 g, 5.5 mmol) in CH_2Cl_2 (50 cm^3) and methanol[29] (1 cm^3) at −80 °C was passed O_2 for 10 min, ozonised O_2 for 40 min and then N_2 until the blue colouration of dissolved ozone had disappeared. Me_2S[30] (4 cm^3) was added and the mixture allowed to warm to room temperature over 3 h, when it was washed (water), extracted (CH_2Cl_2) and the extract was dried (Na_2SO_4) and evaporated. Purification by flash chromatography (hexane–EtOAc, 5:1) yielded 2-benzyloxy-2-cyclohexylethanal **18**[13] as a colourless liquid pure by TLC (545 mg, 43%); δ_H(60 MHz)

0.90–2.00 (11 H, m, c-Hex), 3.33–3.50 (1 H, dd, *J* 4, 5, OCH), 4.50 (2 H, ABq, *J* 6, CH_2Ph), 7.23 (5 H, M, Ph) and 9.50 (1 H, d, *J* 4, CHO).

To a solution of the aldehyde **18** (464 mg, 2 mmol) and allyltrimethylsilane **8** (456 mg, 4 mmol, 640 mm^3) in CH_2Cl_2 (10 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (16 mm^3, 2 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 10 min. Methanol (1 cm^3) and hydrochloric acid (36%; 7 drops) were added. Analysis by TLC (hexane–Et_2O, 5:3) indicated the desilylation to be complete in 10 min. Work-up (CH_2Cl_2) and purification by flash chromatography (hexane–Et_2O, 4:1) gave a mixture of alcohols **19** and **20** as a colourless liquid (412 mg, 75%; ratio 1.5:1 by ^{1}H NMR). A sample for microanalysis was purified by distillation; b.p. (oil bath) 110 °C/0.005 mmHg (Found: C, 78.8; H, 9.8. $C_{18}H_{26}O_2$ requires C, 78.8; H, 9.55%); ν_{max}(liquid film)/cm^{-1} 3420, 1680, 1600 and 1560; δ_H(300 MHz) 1.05–1.40, 1.60–2.05 (11 H, m, c-Hex), 2.20–2.50 (3 H, m, O*H* + CH_2CH=CH_2), 3.09 (0.4 H, dd, *J* 3.6, 5.8, *H*COCH$_2$Ph, *l*), 3.21 (0.6 H, t, *J* 5.2, *H*COCH$_2$Ph, *u*), 3.73 (0.4 H, m, *H*COH, *l*), 3.80 (0.6 H, m, *H*COH, *u*), 4.58 (0.4 H, d, *J* 11.1, PhCH_2, *l*), 4.62 (0.6 H, d, *J* 11.3, PhCH_2 *u*), 4.67 (0.4 H, d, *J* 11.1, PhCH_2, *l*), 4.69 (0.6 H, d, *J* 11.3, PhCH_2, *u*), 5.05–5.20 (2 H, m, CH=CH_2), 5.75–6.00 (1 H, m, C*H*=CH$_2$) and 7.35 (5 H, 2 s, Ph) [lit.,[31] for *l*-isomer **20** δ_H 3.09 (dd, *J* 5.6, 3.2), 3.74 (m)]; δ_C(75.5 MHz) 26.2, 26.3, 26.5 (3 C), 28.5, 28.6, 30.1, 30.3 (c-HexCH$_2$), 36.9, 39.5 (*C*H$_2$CH=CH$_2$), 39.9, 40.2 (c-Hex*C*H), 70.6, 71.0 (COH), 74.9 (*C*H$_2$Ph), 85.6, 86.8 (*C*OCH$_2$Ph), 117.2, 117.9 (C=*C*H$_2$), 127.6, 127.7, 128.4 (2 C, Ph*C*H), 135.1, 135.4 (*C*H=CH$_2$) 138.5, 138.8 (Ph*C*).

anti(u)- *and* syn(l)-1-*Benzoyloxy*-1-*cyclohexylpent*-4-*en*-2-*ol* **22** *and* **23**.—To a solution of 1-cyclohexylprop-2-en-1-ol[26,27] (1.4 g, 10 mmol) in pyridine (10 cm^3) was added benzoyl chloride (1.4 g, 10 mmol, 1.14 cm^3). The mixture was refluxed for 1 h and then put onto ice (100 g), extracted (CH_2Cl_2, 3 × 75 cm^3) and the combined extracts were washed (saturated aqueous $NaHCO_3$) and dried (Na_2SO_4). Evaporation of solvent and purification by flash chromatography (hexane–EtOAc, 10:1) yielded 3-benzoyloxy-3-cyclohexylprop-1-ene as a colourless liquid, pure by TLC (2.28 g, 93%); δ_H(60 MHz) 0.85–2.00 (11 H, m, c-Hex), 5.00–5.45 (3 H, m, OC*H* + CH=CH_2), 5.60–6.10 (1 H, m, C*H*=CH$_2$), 7.15–7.60 (3 H, m, Ph) 7.80–8.20 (2 H, m, Ph). Through a solution of this material (2.28 mg, 9.3 mmol) in CH_2Cl_2 (50 cm^3) and methanol (0.7 cm^3) at −80 °C was passed O_2 for 10 min, ozonised O_2 for 40 min and then O_2 for 10 min. Et_3N[29] (5 cm^3) was added and the mixture allowed to warm up to room temperature over 1 h, when it was washed with water, extracted with Et_2O and the extract was dried (Na_2SO_4) and evaporated. Purification by flash chromatography (hexane–EtOAc, 4:1) yielded 2-benzoyloxy-2-cyclohexylethanal **21** as a colourless liquid pure by TLC and NMR (1.88 g, 82%); δ_H(300 MHz) 0.90–2.10 (11 H, m, c-Hex), 5.06 (1 H, dd, *J* 0.9, 5.0, OCH), 7.40–7.65 (3 H, m, Ph), 8.05–8.15 (2 H, m, Ph) and 9.65 (1 H, d, *J* 1.0, CHO).

To a solution of the aldehyde **21** (1.23 g, 5 mmol) and allyltrimethylsilane **8** (1.14 g, 10 mmol, 1.60 cm^3) in CH_2Cl_2 (25 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (20 mm^3, 2.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be essentially complete in 1 day. Work-up (Et_2O) and purification by flash chromatography (hexane–Et_2O, 7:3) yielded a mixture of alcohols **22** and **23** (1.18 g, 82%; ratio *ca.* 1:1 by ^{13}C NMR). A sample for microanalysis was purified by distillation; b.p. (oil bath) 140 °C/0.005 mmHg (Found: C, 75.2; H, 8.4. $C_{18}H_{24}O_3$ requires C, 75.0; H, 8.4%). ν_{max}(liquid film)/cm^{-1} 3500, 1700, 1625, 1600 and 1580; δ_H(300 MHz) 1.05–1.40, 1.60–2.05 (11 H, m, c-Hex), 2.05–2.45 (3 H, m, O*H* + CH_2CH=CH$_2$), 3.95 (1 H, m, *H*COH), 4.95 (0.5 H, dd, *J* 3.3, 7.8, *H*COCOPh), 5.04 (0.5 H, t, *J* 5.6, *H*COCOPh), 5.05–5.20 (2 H, m, CH=CH_2), 5.75–6.00 (1 H, m, C*H*=CH$_2$), 7.40–7.50 (2 H, m, *m*-Ar), 7.50–7.60 (1 H, m, *p*-Ar) and 8.00–8.15 (2 H, m, *o*-Ar); δ_C(75.5 MHz) 25.8, 25.9, 26.1, 26.2, 27.6, 28.5, 29.5, 29.9 (c-HexCH$_2$), 37.1, 38.9 (*C*H$_2$CH=CH$_2$), 38.4, 38.7 (c-HexCH), 69.7, 69.9 (COH), 80.2, 80.4 (*C*OCOPh), 118.2, 118.5 (CH=*C*H$_2$), 128.4, 129.6, 129.7 (2 C), 133.0, 134.1, 134.5, 140.4 (Ph*C*H), 130.0, 130.1 (Ph*C*), 166.4 and 166.6 (C=O).

2-*Methyl*-3-*benzyloxypropanal* **24**.—To a suspension of pyridinium chlorochromate (0.55 g, 2.5 mmol) in CH_2Cl_2 (6 cm^3) at room temperature was added a solution of 3-benzyloxy-2-methylpropan-1-ol[11] (0.3 g, 1.7 mmol) in CH_2Cl_2 (5 cm^3). After 2 h, Et_2O (20 cm^3) was added, the resulting solution was decanted from the residue and the residue was extracted with a further portion of Et_2O (20 cm^3). The extracts were combined and filtered through Celite and then evaporated to yield a crude mixture (0.5 g) which was purified by flash chromatography (hexane–Et_2O, 5:1) to give the aldehyde **24** as a pale yellow liquid, pure by TLC (255 mg, 86%); δ_H(300 MHz) 1.12 (3 H, d, *J* 7.1, Me), 2.67 (1 H, m, MeC*H*), 3.65 (2 H, m, OCH_2CHMe), 4.52 (2 H, s, CH_2Ph), 7.32 (5 H, br s, Ph) and 9.72 (1 H, d, *J* 1.5, CHO) [lit.,[11] δ_H 1.14 (3 H, d, *J* 7), 2.65–2.68 (1 H, m), 3.67 (2 H, m), 4.53 (2 H, s), 7.33 (5 H, s) and 9.73 (1 H, s)].

Reaction of 3-*Benzyloxy*-2-*methyl*-3-*propanal* **24** *with Allyltrimethylsilane* **8** *Catalysed by* $TfOH_2^+B(OTf)_4^-$.—To a solution of the aldehyde **24** (354 mg, 2 mmol) and allyltrimethylsilane **8** (456 mg, 4 mmol, 640 mm^3) in CH_2Cl_2 (15 cm^3) at −40 °C was added $TfOH_2^+B(OTf)_4^-$ (20 mm^3, 2.5 mol%). The mixture was left at −40 °C for 2.25 h. Work-up (CH_2Cl_2) and flash chromatography (hexane–Et_2O, 5:3) gave (*l*)- and (*u*)-1-benzyloxy-2-methylhex-5-en-3-ol **25** and **26** as a colourless liquid, pure by TLC (227 mg, 52%; ratio 1.8:1 by ^{1}H NMR); δ_H(300 MHz) 0.91 (*u*), 0.95 (*l*) (3 H, d, *J* 7, Me), 1.80–2.00 (1 H, m, MeC*H*), 2.12–2.40 (2 H, m, CH_2CH=CH$_2$), 3.44–3.60 (3 H, m, O*H* + OCH_2CHMe), 3.88–3.95 (1 H, m, OCH), 4.50 (2 H, s, CH_2Ph), 5.00–5.20 (2 H, m, CH=CH_2), 5.75–6.00 (1 H, m, C*H*=CH$_2$) and 7.20–7.40 (5 H, m, Ph); δ_C(75.5 MHz) 10.6 (*l*), 13.7 (*u*), 37.4 (*l*), 37.8 (*u*), 38.8 (*l*), 39.3 (*u*), 72.8, 73.3, 74.4, 74.6, 74.8, 117.1, 127.5, 128.3, 135.1 (*u*), 135.5 (*l*), 137.8 (*u*) and 138.0 (*l*); [lit.,[11] δ_C(*u*) 13.6, 37.7, 39.1 and 135.0; (l): 10.5, 37.3, 38.7 and 135.4].

Reaction of 3-*Benzyloxy*-2-*methylpropanal* **24** *with Allyltrimethylsilane* **8** *Catalysed by Iodotrimethylsilane*.—To a solution of the aldehyde **24** (255 mg, 1.43 mmol) and allyltrimethylsilane **8** (326 mg, 2.86 mmol, 458 mm^3) in CH_2Cl_2 (10 cm^3) was added a solution of iodotrimethylsilane (0.2 mol dm^{-3}; 1.43 cm^3, 20 mol%; prepared by the addition of I_2 to a solution of compound **8** in CH_2Cl_2).[32] Analysis by TLC (hexane–Et_2O, 5:3) indicated complete disappearance of compound **24** in 25 min. The mixture was washed (saturated aqueous $Na_2S_2O_3$), extracted (CH_2Cl_2), dried (Na_2SO_4) and evaporated. Purification by flash chromatography (hexane–Et_2O, 5:3) yielded the alcohols **25** and **26** contaminated with unidentified impurities (176 mg; estimated as *ca.* 30% yield, isomeric ratio 1.4:1, by ^{1}H NMR).

Reaction of Benzaldehyde **9f** *with* 1-*Trimethylsilylbut*-2-*ene* **29** *Catalysed by* $TfOH_2^+B(OTf)_4^-$.—To a solution of benzaldehyde **9f** (106 mg, 1 mmol, 100 mm^3) and 1-trimethylsilylbut-2-ene **29** (*E*:*Z*, 85:15; synthesised by the method of Hayashi *et al.*)[14] (256 mg, 2 mmol, 340 mm^3) in CH_2Cl_2 (4 cm^3) was added $TfOH_2^+B(OTf)_4^-$ (2 mm^3, 0.5 mol%). Analysis by TLC (hexane–Et_2O, 5:3) indicated the reaction to be complete in 5 min. Work-up (CH_2Cl_2) and purification by flash chromatography (hexane–Et_2O, 3:2) gave 2-methyl-1-phenylbut-3-en-1-ol as a colourless liquid, pure by TLC and NMR (141 mg, 86%;

syn:*anti*, 65:35 by ^{1}H NMR); δ_H(300 MHz) 0.86 (*anti*), 1.00 (*syn*) (3 H, d, *J* 6.8, Me), 2.10 (*syn*), 2.25 (*anti*) (br s, OH), 2.40–2.65 (1 H, m, MeC*H*), 4.35 (*anti*, *J* 7.8), 4.55 (*syn*, *J* 5.5), (1 H, d, OCH), 4.95–5.20 (2 H, m, CH=CH_2), 5.65–5.85 (1 H, m, C*H*=CH_2) and 7.20–7.40 (5 H, m, Ph) [lit.,[33,34] δ_H(100 MHz, CCl_4) 0.84 (*anti*), 0.93 (*syn*), (3 H, d, *J* 7), 2.00 (*syn*), 2.84 (*anti*, br s, OH), 2.36 (*anti*) 2.44 (*syn*, 1 H, m), 4.24 (*anti*, *J* 8), 4.40 (*syn*, *J* 6) (1 H, d), 4.80–5.10 (2 H, m), 5.48–5.82 (1 H, m), 7.14 (5 H, br s)]. Traces of 1-phenylpent-3-en-1-ol (< 1%) could be detected by the presence of a doublet at δ 1.67.

Acknowledgements

This work was supported in part by the SCIENCE programme of the European Community. We are grateful to Dr. M. G. Orchard for helpful discussions, and to Prof. G. E. Keck for spectroscopic data relating to alcohol **20**. The molecular modelling facility used for the MO calculations was funded by EOLAS (the Irish science and technology agency) and Loctite Corp.

References

1 (*a*) H. Sakurai, *Pure Appl. Chem.*, 1982, **54**, 1; (*b*) I. Fleming, J. Dunoguès and R. Smithers, *Org. React.* (*N.Y.*), 1989, **37**, 57, and refs. cited therein.
2 Preliminary communication; A. P. Davis and M. Jaspars, *J. Chem. Soc., Chem. Commun.*, 1990, 1176.
3 (*a*) R. Calas, J. Dunoguès, G. Deleris and F. Pisciotti, *J. Organomet. Chem.*, 1974, **69**, C15; (*b*) E. W. Abel and R. J. Rowley, *J. Organomet. Chem.*, 1975, **84**, 199; (*c*) G. Deleris, J. Dunoguès and R. Calas, *J. Organomet. Chem.*, 1975, **93**, 43; (*d*) A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 1976, 1295.
4 N. Iwasawa and T. Mukaiyama, *Chem. Lett.*, 1987, 463.
5 S. E. Denmark, B. R. Henke and E. Weber, *J. Am. Chem. Soc.*, 1987, **109**, 2512.
6 T. Mukaiyama, H. Nagaoka, M. Murakami and M. Ohshima, *Chem. Lett.*, 1985, 977.
7 A. Hosomi, A. Shirahata and H. Sakurai, *Tetrahedron Lett.*, 1978, 3043.
8 D. Schinzer, *Synthesis*, 1988, 263.
9 (*a*) A. Engelbrecht and E. Tschager, *Z. Anorg. Allg. Chem.*, 1977, **433**, 19; (*b*) G. A. Olah, K. Laali and O. Farooq, *J. Org. Chem.*, 1984, **49**, 4591.
10 For the use of $TfOH_2^+B(OTf)_4^-$ to initiate reactions on unfunctionalised hydrocarbons, see ref. 9*b* and; G. A. Olah, O. Farooq, V. V. Krishnamurthy, G. K. Surya Prakash and K. Laali, *J. Am. Chem. Soc.*, 1985, **107**, 7541; O. Farooq, S. M. F. Farnia, M. Stephenson and G. A. Olah, *J. Org. Chem.*, 1988, **53**, 2840.
11 C. H. Heathcock, S. Kiyooka and T. Blumenkopf, *J. Org. Chem.*, 1984, **49**, 4214.
12 M. T. Reetz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 556.
13 G. E. Keck and E. P. Boden, *Tetrahedron Lett.*, 1984, **25**, 265.
14 T. Hayashi, K. Kabeta, I. Hamachi and M. Kumada, *Tetrahedron Lett.*, 1983, **24**, 2865.
15 T. Morita, Y. Okamoto and H. Sakurai, *Synthesis*, 1981, 745.
16 M. Fujita and T. Hiyama, *J. Org. Chem.*, 1988, **53**, 5415.
17 A. P. Davis and M. Jaspars, *Angew. Chem.*, 1992, **104**, 475; *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 470.
18 *Dictionary of Organic Compounds*, ed. J. Buckingham, Chapman and Hall, London, 5th ed. vol. 4, p. 4385.
19 D. Seebach, R. Imwinkelried and G. Stucky, *Helv. Chim. Acta*, 1987, **70**, 448.
20 R. W. Hoffmann and T. Herold, *Chem. Ber.*, 1981, **114**, 375.
21 N. Minowa and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 3697.
22 G. P. Chiusoli, G. Salerno, U. Bersellini, F. Dallatomasina and S. Preseglio, *Transition Met. Chem.* (*Weinheim, Ger.*), 1978, **3**, 174.
23 A. Hosomi, S. Kohra, K. Ogata, T. Yanagi and Y. Tominaga, *J. Org. Chem.*, 1990, **55**, 2415.
24 J. A. Katzenellenbogen and R. S. Lenox, *J. Org. Chem.*, 1973, **38**, 326.
25 Y. Yamamoto, H. Yatagai, Y. Ishihara, N. Maeda and K. Maruyama, *Tetrahedron*, 1984, **40**, 2239.
26 D. Seyferth, *Org. Synth.*, 1959, **39**, 10.
27 P. A. Aristoff, P. D. Johnson and A. W. Harrison, *J. Am. Chem. Soc.*, 1985, **107**, 7967.
28 S. Czernecki, C. Georgoulis and C. Provelenghiou, *Tetrahedron Lett.*, 1976, 3535.
29 R. M. Ellam and J. M. Padbury, *J. Chem. Soc., Chem. Commun.*, 1971, 1094.
30 J. J. Pappas, W. P. Keaveney, E. Gancher and M. Berger, *Tetrahedron Lett.*, 1966, 4273.
31 E. P. Boden, Ph.D. Thesis, University of Utah; G. E. Keck, personal communication.
32 M. E. Jung and T. A. Blumenkopf, *Tetrahedron Lett.*, 1978, 3657.
33 T. Hiyama, K. Kimura and H. Nozaki, *Tetrahedron Lett.*, 1981, **22**, 1037.
34 Y. Yamamoto, H. Yatagai and K. Maruyama, *J. Am. Chem. Soc.*, 1981, **103**, 1969.

Paper 2/01348G
Received 13*th March* 1992
Accepted 12*th May* 1992