Stereocontrol in organic synthesis using silicon-containing compounds. Syntheses of (±)-2-deoxyribonolactone and (±)-arabonolactone

Ian Fleming * and Sunil K. Ghosh

Department of Chemistry, Lensfield Road, Cambridge, UK CB2 1EW

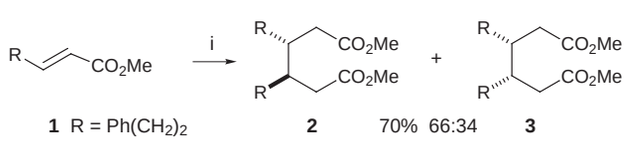
Samarium iodide reacts with methyl (*Z*)-3-dimethyl(4-methylphenyl)silylprop-2-enoate 5b to give dimethyl (3*RS*,4*SR*)-3,4-bis[dimethyl(4-methylphenyl)silyl]hexane-1,6-dioate 8b with high stereoselectivity. This *meso* diester can be converted into (3*RS*,4*SR*)-3,4-bis[dimethyl(4-methylphenyl)silyl]-pentan-5-olide 16 by Dieckmann cyclisation, demethoxycarbonylation and Baeyer–Villiger reaction. Silyl-to-hydroxy conversion and relactonisation gave (±)-deoxyribonolactone, and *anti*-selective enolate hydroxylation followed by silyl-to-hydroxy conversion gave (±)-arabonolactone. An attempt to synthesise sugars with the relative configuration (3*RS*,4*RS*) was thwarted by an unprecedented retention of configuration at the migration origin in the cationic rearrangement of (3*RS*,4*SR*)-3,4-bis[dimethyl(4-methylphenyl)silyl]-5-hydroxypentanoic acid 28 to (3*RS*,4*SR*)-3,5-bis[dimethyl(4-methylphenyl)silyl]pentan-1,4-olide 30.

Introduction

In order to extend the power of our silicon-based methods to the synthesis of target molecules having more than the three or four stereogenic centres present in the syntheses described so far, we wanted to be able to set up starting materials possessing two (or more) silicon-bearing centres related to each other. We could also see that it would give us greater scope if the two silicon-bearing centres were available in compounds having them 1,2-related, 1,3-related and 1,4-related, and all these molecules should also have terminal functionality, with which to transfer stereochemical information out along each chain. We have already reported a method for setting up 1,3-related, silicon-bearing centres,[1] and the following paper[2] describes a method for setting them up 1,4-related. We now describe in full the synthesis of the diester **8b** with the two centres 1,2-related, enlarging on two preliminary communications.[3] Having a compound with 1,2-related silicon-bearing centres, and knowing that both silyl groups could be converted into hydroxy groups, we were naturally attracted to the possibility of using it to synthesise sugars, which we did, not only to demonstrate this capacity, but also to confirm the stereochemical relationship in the diester **8b** that we had prepared. In the last paper in this series, we report a synthesis of nonactin from the same diester.

Results and discussion

Inanaga reported that samarium(II) iodide in THF–HMPA containing one equivalent of *tert*-butyl alcohol induced the reductive coupling of β-substituted acrylic acid derivatives like **1**, giving 3,4-disubstituted adipic acid derivatives **2** and **3** in favour (2:1) of the *racemic* diastereoisomer **2** (Scheme 1).[4]

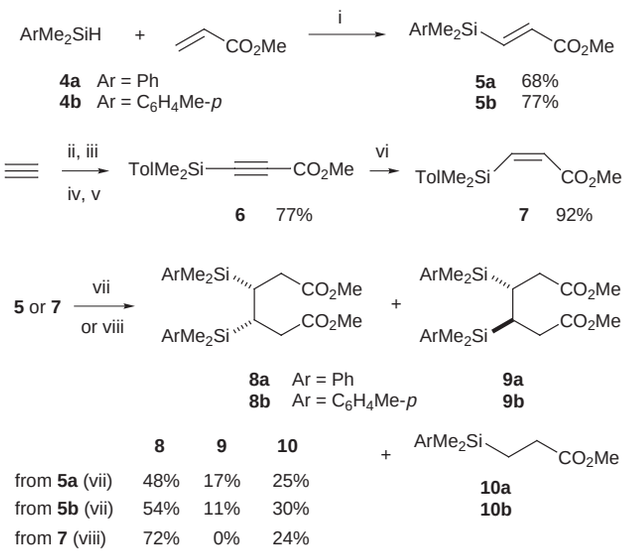


1 R = $Ph(CH_2)_2$ **2** 70% 66:34 **3**

Scheme 1 *Reagents*: i, SmI_2, THF, HMPA, Bu^{t}OH

More recently, Alper has reported that he saw no reductive coupling in HMPA alone, only reduction of the C=C double bond.[5]

If the stereoselectivity could be improved, and if the reaction would work for β-silylacrylic esters, this promised to be ideal for the synthesis of compounds having the two silyl groups 1,2-related and providing suitably versatile functionality at both ends of the chain. We prepared the *trans* acrylic esters **5** by hydrosilylation of methyl acrylate using dicobalt octacarbonyl as the catalyst,[6] and the *cis* ester **7** by silylation of ethynylmagnesium bromide with tolyldimethylsilyl chloride followed by methoxycarbonylation and catalytic hydrogenation (Scheme 2).

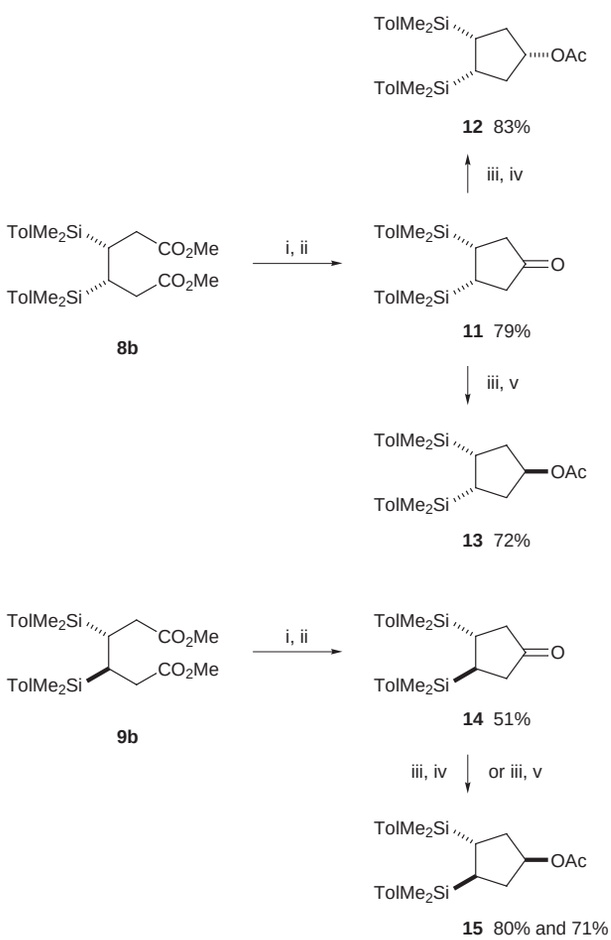


Scheme 2 *Reagents*: i, $Co_2(CO)_8$ cat., $ArSiMe_2H$; ii, EtMgBr; iii, $TolMe_2SiCl$; iv, BuLi; v, MeO_2CCl; vi, H_2, $Pd/BaSO_4$, quinoline; vii, SmI_2, THF, HMPA, Bu^{t}OH; viii, SmI_2, THF, DMPU, dimethyl malonate

In agreement with Inanaga, we found that they gave the adipate esters **8** and **9** by reductive coupling as the major pathway, and in part agreement with Alper, there was also some apparently unavoidable reduction of the C=C double bond giving the esters **10** (Scheme 1). However, in contrast to Inanaga, the β-silylated acrylic esters **5** and **7** favoured the *meso* diastereoisomers **8**. The phenyldimethylsilyl-containing product **8a** was crystalline, but low melting (mp 41–42 °C), and so we tried the tolyldimethylsilyl group. This group proved to have the advantage over the phenyldimethylsilyl group of imparting a higher melting point to the product **8b**, and it should also prove to be somewhat easier to remove in our silyl-to-hydroxy conversion. It has the

disadvantage that we have been unable to make the corresponding silyllithium reagent from the chloride,[7] but we did not need a silyllithium or cuprate reagent for the preparation of either the *cis* or the *trans* acrylic esters **7** or **5b**. We tried several combinations of solvent, geometry of starting material, and conditions of coupling, and find that the best, at least for our substrates, was to use the *cis* ester **7** in 6:1 THF–DMPU, which was better than Inanaga's THF–HMPA, with one equivalent of freshly prepared samarium iodide at 20 °C, and with three equivalents of dimethyl malonate as the proton source, which was better than his *tert*-butyl alcohol. These conditions gave the easily purified *meso* diester **8b**, mp 96–97 °C, in 72% yield, together with 24% of methyl 3-dimethyl(*p*-tolyl)silylpropanoate, but with no trace of the *racemic* diastereoisomer **9b**, even in the crude reaction mixture.

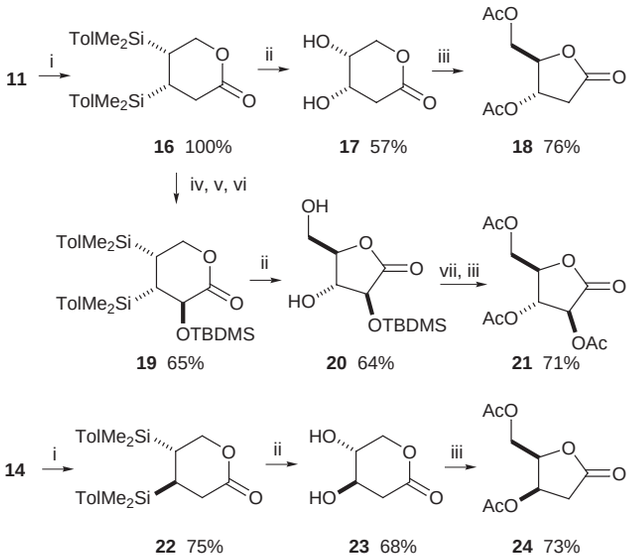
We proved the relative stereochemistry of the major **8b** and minor **9b** diastereoisomers by the sequence of reactions in Scheme 3. Dieckmann cyclisation of the major product and



Scheme 3 *Reagents*: i, LDA; ii, NaCl, DMSO, H_2O; iii, $NaBH_4$; iv, Ac_2O; v, AcOH, DEAD, Ph_3P

Krapcho demethoxycarbonylation[8] gave the cyclopentanone **11**, and we were able to make its diastereoisomer **14** from the racemic diester isolated as the minor product in our exploratory work on the reductive coupling. The cyclopentanone **11** gave a 93:7 mixture of two acetates **12** and **13** on reduction with sodium borohydride followed by acetylation. Alternatively, reduction with sodium borohydride, followed by Mitsunobu reaction[9] using acetic acid, gave the acetates **12** and **13** in a ratio of 7:93. In contrast, the cyclopentanone **14** gave a single acetate **15** on reduction with sodium borohydride followed by acetylation, and Mitsunobu reaction on the intermediate alcohol returned the same acetate.

We used the cyclopentanone **11** to synthesise (±)-deoxyribonolactone and its acetate **18**, and the acetate **21** of (±)-



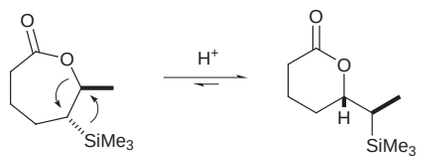
Scheme 4 *Reagents*: i, MCPBA, Na_2HPO_4; ii, KBr, NaOAc, AcOOH; iii, Ac_2O, $HClO_4$; iv, NaHMDS, THF; v, 2-phenylsulfonyl-3-phenyloxaziridine; vi, TBDMSCl, imidazole; vii, TBAF, THF

arabonolactone, as shown in Scheme 4. For this purpose, we prepared the cyclopentanone **11** in a slightly better overall yield (57%) by carrying out the samarium coupling on the *E*-acrylic ester **5b** in 6:1 THF–DMPU in the absence of a proton source, but quenching with *tert*-butyl alcohol. This gave a mixture of the Dieckmann cyclisation product and the diester **8b**, directly in 70% yield in a ratio of 8:2, which could no doubt have been raised by longer treatment with butoxide ion. We submitted the mixture to the conditions of the Krapcho reaction to get the ketone **11**, now easily separable from the diester. Baeyer–Villiger reaction on the ketone **11** gave the lactone **16**. Conversion of the silyl to hydroxy groups using potassium bromide in buffered peracetic acid[10] gave the lactone alcohol **17**, which rearranged in acid to give the corresponding γ-lactone. Acetylation gave the known acetate **18** with a ^1H NMR spectrum identical with that reported. Davis hydroxylation[11] of the lactone **16** followed by silylation gave the lactone **19**, which we converted to the arabonolactone acetate **21**, with a ^{13}C NMR spectrum identical with that reported,[12] by way of the γ-lactone **20**. By a suitable combination of protection and Mitsunobu or equivalent reactions, all the pentose lactones and 2-deoxypentose lactones, and hence pentoses, are, in principle, available from the diol **17** and the triol ether **20**.

However, it would avoid several of the Mitsunobu reactions, and much complication, if we could make the racemic diester **9b**, having the (3*RS*,4*RS*) relative configuration, as easily as we can make the *meso* diester **8b**, having the (3*RS*,4*SR*) relative configuration. So far, we have been unable to find conditions in which the liquid diastereoisomer **9b** was the major product—at best, using 6:1 THF–HMPA, and one equivalent of *tert*-butyl alcohol as the proton source, we obtained 60% of the adipic esters **8b** and **9b** in a ratio of 70:30, and isolated the racemic adipate **9b** from this mixture in only 14% overall yield (Scheme 2). Nevertheless, we were able to show that this compound could be a starting material for the synthesis of the family of (3*RS*,4*RS*)-sugars. We repeated the same sequence of Dieckmann and Krapcho reactions to give the cyclopentanone **14**, Baeyer–Villiger reaction to give the lactone **22**, silyl-to-hydroxy conversion to give the diol lactone **23**, and isomerisation and acetylation to give acetate **24**.[13]

These three pentose syntheses are of course, of racemic sugar derivatives. To make the first two **18** and **21** enantiomerically enriched, we needed to find a method for desymmetrising the *meso* ketone **11**, and have done so[14] using Simpkins' chiral base.[15] The degree of the desymmetrisation was excellent, but the sense in which it took place has not yet been established.

Because we had not been able to prepare the diester **9b** in good yield, we sought an alternative route to the pentose lactone **22** in the (3*RS*,4*RS*) series, avoiding the cyclopentanone **14**. One way of overcoming this limitation might be to take advantage of Hudrlik's observation[16] that lactones with an embedded silylethylcarboxylate group sometimes undergo acid-catalysed rearrangement, with inversion of configuration at both sites, as in the example **25** ⟶ **26**.



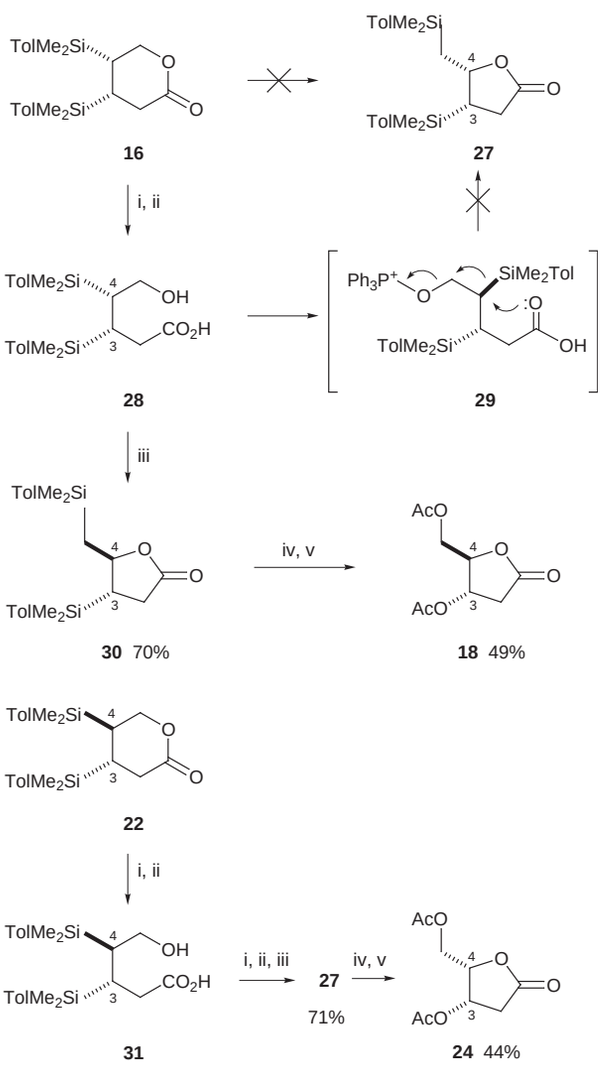
25 **26**

Not too surprisingly, we were not able to persuade the δ-lactone **16**, to rearrange to the γ-lactone **27**, presumably because the δ-lactone is thermodynamically the more stable isomer, although we had hoped that steric repulsion between the *cis*-disposed silyl groups in the lactone **16** might have disturbed this pattern. To overcome this difficulty, we opened the lactone to give the γ-hydroxy acid **28**, and submitted it to Mitsunobu conditions without an external nucleophile, hoping that the kinetic preference for five-membered ring-formation might set off the [1,2]-sigmatropic silyl shift, **29** arrows (Scheme 5). We found that the hydroxy acid **28** did indeed give largely (typically 85:15) a γ-lactone in competition with a relactonisation **28** ⟶ **16** that we could not completely suppress, but the γ-lactone **30** that we obtained did not have the stereochemistry **27** that we had expected by analogy with Hudrlik's work.

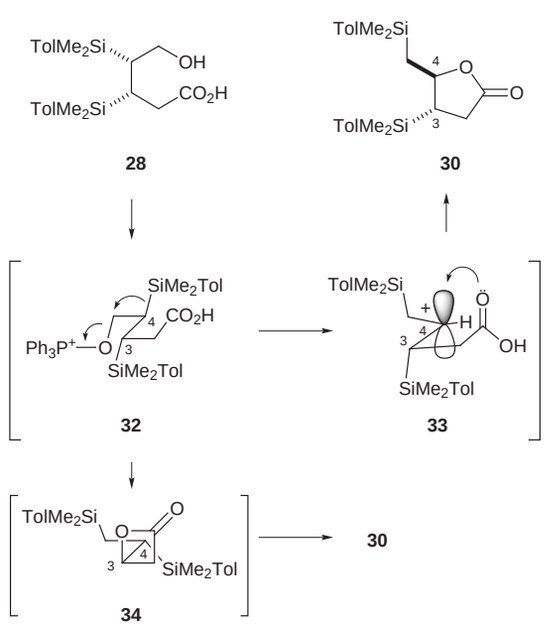
We proved the relative configuration in the lactone **30** by converting the silyl groups to hydroxy groups, in a reaction taking place reliably with retention of configuration,[10] and acetylating the product to give (±)-deoxyribonolactone diacetate **18**, immediately recognisable, and distinguishable from the diastereoisomer **24**, which we expected and had already prepared. To test whether we were observing simply the loss of stereochemical integrity at C-4, which does have precedent,[17] we repeated this sequence of reactions using the diastereoisomeric δ-lactone **22**, and obtained, in addition to the usual product of unavoidable (typically 16%) relactonisation **31** ⟶ **22**, successively the γ-lactone **27** and (±)-deoxyxylonolactone diacetate **24**. (In order to illustrate the connection between the lactones **22**, **27** and **24**, we have drawn the former in Scheme 5 as the enantiomer of the drawing in Scheme 4.) We did not detect (TLC, ^{1}H NMR) any cross contamination in the two series. Clearly the rearrangement is strictly stereospecific, with retention of configuration at the migration origin, C-4, a remarkable event that is, we believe, without precedent in cationic rearrangements.

One possible explanation we raise only to dismiss. Hudrlik, knowing the relative configuration in the lactone **25**, had proved the relative configuration in the lactone **26** by converting the hydroxy acid derived from it into the corresponding *trans* alkene with boron trifluoride–diethyl ether and into the *cis* alkene with potassium hydride, in reactions known to be stereospecifically *anti* and *syn*, respectively. Strictly speaking, this is compatible with double retention as well as with the double inversion shown in **25** ⟶ **26**. Dyotropic rearrangements of this type with double retention or double inversion are forbidden to be concerted by the Woodward–Hoffmann rules,[18] and are most likely therefore stepwise ionic processes, as the need for acid catalysis attests. Naturally Hudrlik chose to illustrate his reaction as a double inversion, with which we concur, because it seems extraordinarily unlikely that a nucleophilic displacement of carboxylate at the migration terminus should take place with retention of configuration.

We believe that the silyl groups in the intermediate **29** will be disposed conformationally *anti* **32** at the time of rearrangement, and that the cation **33** is an intermediate (Scheme 6). This cation is highly stabilised, with silicon–carbon bonds over-



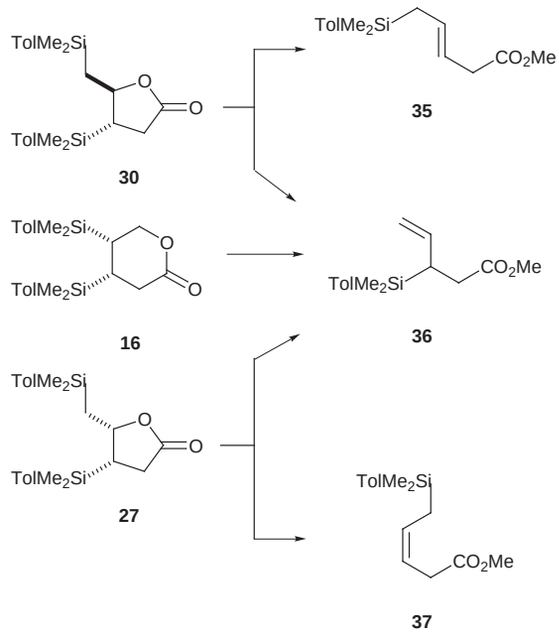
Scheme 5 *Reagents*: i, KOH, MeOH; ii, citric acid; iii, DEAD, Ph_3P, CH_2Cl_2; iv, KBr, AcOOH, AcOH; v, Ac_2O, $HClO_4$



Scheme 6

lapping with the empty p-orbital on both surfaces of the trigonal carbon, thus driving the rearrangement step without any need for nucleophilic participation. Given that a nucleophile could attack this cation *anti* to a silyl group on either surface, it is not at first sight obvious why we observe a high level of stereospecificity rather than a low level of stereoselectivity. We suggest that restricted rotation about the bond between C-3 and C-4 ensures that the carboxylic acid group is held above the plane of the trigonal carbon, as drawn, thus ensuring the delivery of the nucleophile, **33** arrow, to the same surface from which the silyl group had departed. The same argument, applied to the hydroxy acid **31**, leads to the lactone **27**. One other possibility is that the ionisation and rearrangement (**32** arrows) are concerted with a shift of the C-3 silyl group, and the capture of a C-3 ion by the carboxylate to give the β-lactone **34**. This attractive pathway takes place with a graceful sequence of unexceptionable inversions of configuration at each centre. We were unable to detect (IR) any β-lactone in our mixtures, although we looked for it immediately after the reagents had been mixed, by which time the reaction was effectively over. Furthermore, it is hard to see how the β-lactone could rearrange to the γ-lactone **30**, with a symmetry-forbidden inversion at both centres, except by a stepwise pathway, by way of the very cation **33** that is the basis for our earlier explanation. The critical point here is that it is not obviously reasonable for a reaction pathway to avoid the intermediate β-silyl cation **33** in going from the alcohol **28** to the β-lactone **34**, only to use it to get from the β-lactone to the γ-lactone **30**. This pathway remains a possibility, but it seems to us unlikely. The nearest analogy to the event taking place at C-4 in our reaction is the retention of configuration sometimes observed in S_N1 reactions of chiral halides and sulfonates in which nucleophilic participation by a neighbouring group preserves stereochemical information in the intermediate cation.[19] Retention of configuration at the migration terminus in a cationic rearrangement, in which a β-silyl group preserves configuration, has also been observed recently,[20] complementing our results here, in which the retention is at the migration origin. We prefer to avoid bridged structures for the β-silyl cations—they are certainly unnecessary,[21] except as transition structures for the 1,2-shifts.

With two silyl groups β to the carboxylate group in the lactones **30** and **27**, we wondered which would be captured by fluoride ion on treatment with tetrabutylammonium fluoride (TBAF) or boron trifluoride–diethyl ether. Baldwin's rules suggest that endocyclic elimination ought not to be favoured, since it is the reverse of a 5-*endo*-*trig* process.[22] We find, however, that the lactone **30** with TBAF gives more endocyclic elimination **30** ⟶ **35** than exocyclic **30** ⟶ **36**, although the lactone **27** does give marginally more exocyclic elimination (Scheme 7). However, both lactones give mainly endocyclic elimination with boron trifluoride–diethyl ether. We suggest that these eliminations, especially that catalysed by boron trifluoride, is an E1 reaction, with a cation like **33** as an intermediate, thus avoiding the strictures of Baldwin's rule. The formation of the more-substituted alkenes **35** and **37** is then unexceptional.[23] This observation is further support for the explanation that we suggest in Scheme 6. The lactone **16** also gave mixtures of the esters **35** and **37** under acidic conditions, but treatment with TBAF gave endocyclic elimination without rearrangement, and provided us with a pure sample of the ester **36**.



Starting material	Conditions	Yield	**35**:**36**:**37**
16	1. TBAF, THF; 2. MeI	94%	0:100:0
16	1. BF_3•OEt_2; 2. CH_2N_2	80%	49:14:37
16	1. RSO_3H; 2. CH_2N_2	60%	44:4:52
30	1. TBAF, THF; 2. MeI	92%	60:39:1
30	1. BF_3•OEt_2; 2. CH_2N_2	85%	76:19:5
27	1. TBAF, THF; 2. MeI	83%	8:51:41
27	1. BF_3•OEt_2; 2. CH_2N_2	93%	4:6:90

Scheme 7

Experimental

Dimethyl(4-methylphenyl)silane 4b

Chlorodimethylsilane (38.0 cm^3, 0.35 mol) was added slowly to 4-methylphenylmagnesium bromide prepared from 4-bromotoluene (60 g, 0.35 mol) and magnesium turnings (8.6 g, 0.354 mol) in ether (200 cm^3) over 1 h and the mixture was refluxed for 10 h. The mixture was filtered, the filtrate evaporated under reduced pressure and the residue distilled to give the *silane* (39.1 g, 75%), bp 68–70 °C/30 mmHg; ν_{max}(film)/cm^{-1} 2140 (SiH), 1250 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.45 (2 H, d, *J* 7.8, Ar), 7.19 (2 H, d, *J* 7.8, Ar), 4.41 (1 H, septet, *J* 3.7, SiH), 2.36 (3 H, s, 4-*Me*C_6H_4) and 0.33 (6 H, d, *J* 3.7, $SiMe_2$); *m*/*z* 150 (41, M^+), 149 (20, M − H) and 135 (100, M − Me) (Found: M^+, 150.0868. $C_9H_{14}Si$ requires *M*, 150.0865).

Chlorodimethyl(4-methylphenyl)silane

4-Methylphenylmagnesium bromide prepared from 4-bromotoluene (70.65 g, 0.413 mol) and magnesium turnings (10.5 g, 0.432 mol) in ether (250 cm^3) was added dropwise to dichlorodimethylsilane (75 cm^3, 0.619 mol) under nitrogen at 0 °C with stirring. After 5 h at reflux, the mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was distilled to give the silane (49.2 g, 65%); bp 89–93 °C/7 mmHg (lit.,[24] 130–131 °C/40 mmHg); ν_{max}(film)/cm^{-1} 1260 (SiMe) and 1120 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.52 (2 H, d, *J* 7.8, Ar), 7.23 (2 H, d, *J* 7.8, Ar), 2.37 (3 H, s, 4-*Me*C_6H_4) and 0.67 (6 H, s, $SiMe_2$), contaminated with about 17% of bromodimethyl-(4-methylphenyl)silane, δ 2.35 (4-*Me*C_6H_4) and 0.81 ($SiMe_2$).

Methyl (*E*)-3-dimethyl(4-methylphenyl)silylprop-2-enoate 5b

Following the method of Sonoda,[6] dimethyl(4-methylphenyl)-silane **4b** (9.0 g, 60 mmol) in benzene (10 cm^3) was added dropwise with stirring to methyl acrylate (25.8 g, 27.0 cm^3, 300 mmol) and dicobalt octacarbonyl (0.82 g, 2.4 mmol) in benzene (50 cm^3) under nitrogen at 25 °C and the mixture kept for 6 h. The solvent was evaporated off under reduced pressure and the residue was taken up in hexane (200 cm^3), filtered through a small pad of silica gel and the filtrate was evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 5:95) to give the *ester* (10.8 g, 77%); R_f(EtOAc–hexane, 5:95) 0.37; ν_{max}(film)/cm^{-1} 1735 (C=O), 1250 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.39 (2 H, d, *J* 7.8, Ar),

7.35 (1 H, d, *J* 18.8, SiC*H*=CH), 7.18 (2 H, d, *J* 7.8, Ar), 6.25 (1 H, d, *J* 18.8, CH=C*H*CO_2Me), 3.73 (3 H, s, OMe), 2.34 (3 H, s, 4-*Me*C_6H_4) and 0.39 (6 H, s, $SiMe_2$); *m*/*z* 234 (47%, M^+), 233 (39, M − H), 219 (100, M − Me), 203 (16, M − OMe) and 149 (42, 4-$MeC_6H_4SiMe_2$) (Found: M^+, 234.1071. $C_{13}H_{18}O_2Si$ requires *M*, 234.1076). The product **5b** is contaminated with methyl 3-dimethyl(4-methylphenyl)silylpropanoate **10b** (8%, by integration of the signals at δ 3.73 and 3.61) characterised below.

Dimethyl(4-methylphenyl)silylethyne

Acetylene was bubbled through dry THF (100 cm^3) while ethylmagnesium bromide (165 cm^3 of a 1 mol dm^{-3} solution in THF) was added dropwise at 0 °C with stirring. After the addition was over, acetylene was passed through the mixture over 1 h at room temperature. A solution of chlorodimethyl(4-methylphenyl)silane (22.8 g, 123.5 mmol) in THF (20 cm^3) was added dropwise at 0 °C and the mixture was refluxed for 15 h. Saturated aqueous ammonium chloride (100 cm^3) was added to the mixture at 0 °C, and the mixture extracted with hexane (3 × 100 cm^3). The extract was washed with water and with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was distilled to give the *acetylene* (18.3 g, 86%); bp 93–94 °C/13 mmHg; R_f(hexane) 0.36; ν_{max}(film)/cm^{-1} 3280 (C≡CH), 2050 (C≡C), 1250 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.53 (2 H, d, *J* 7.8, Ar), 7.21 (2 H, d, *J* 7.8, Ar), 2.50 (1 H, s, C≡CH), 2.36 (3 H, s, 4-*Me*C_6H_4) and 0.43 (6 H, s, $SiMe_2$); *m*/*z* 174 (30%, M^+) and 159 (100, M − Me) (Found: M^+, 174.0876. $C_{11}H_{14}Si$ requires *M*, 174.0865).

Methyl 3-dimethyl(4-methylphenyl)silylprop-2-ynoate 6

Following the method of Solladié,[25] *n*-butyllithium (1.5 mol dm^{-3} in hexane, 50 cm^3) was added dropwise to a stirred solution of the dimethyl(4-methylphenyl)silylethyne (8.5 g, 48.9 mmol) in dry THF (200 cm^3) under nitrogen at −78 °C. After 15 min, methyl chloroformate (10 cm^3, 12.23 g, 129 mmol) was added dropwise over 10 min and the mixture was stirred for 2 h at −78 °C. The temperature was allowed to rise slowly to 0 °C, and the mixture poured into water and extracted with hexane (3 × 125 cm^3). The extract was washed with water and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *ester* (10.1 g, 89%); R_f(EtOAc–hexane, 1:9) 0.4; ν_{max}(film)/cm^{-1} 2210 (C≡C), 1730 (C=O), 1260 (SiMe) and 1120 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.49 (2 H, d, *J* 7.8, Ar), 7.21 (2 H, d, *J* 7.8, Ar), 3.77 (3 H, s, OMe), 2.36 (3 H, s, 4-*Me*C_6H_4) and 0.47 (6 H, s, $SiMe_2$); *m*/*z* 232 (20%, M^+), 217 (7, M − Me), 202 (19, M − 2 × Me) and 189 (100) (Found: M^+, 232.0922. $C_{13}H_{16}O_2Si$ requires *M*, 232.0920).

Methyl (*Z*)-3-dimethyl(4-methylphenyl)silylprop-2-enoate 7

The ester **6** (2.8 g, 12 mmol), quinoline (0.5 cm^3, 546 mg, 4.24 mmol) and palladium (5% on $BaSO_4$, 150 mg) were stirred in toluene (25 cm^3) under hydrogen for 3 h, by which time 270 cm^3 of hydrogen had been absorbed. The mixture was filtered through Celite and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *acrylate* (2.56 g, 92%); R_f(EtOAc–hexane, 1:9) 0.42; ν_{max}(film)/cm^{-1} 1740 (C=O), 1260 (SiMe) and 1120 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.45 (2 H, d, *J* 7.8, Ar), 7.17 (2 H, d, *J* 7.8, Ar), 6.68 (1 H, d, *J* 14.5, CH=C*H*Si), 6.56 (1 H, d, *J* 14.5, CH=C*H*CO_2Me), 3.64 (3 H, s, OMe), 2.34 (3 H, s, 4-*Me*C_6H_4) and 0.45 (6 H, s, $SiMe_2$); *m*/*z* 234 (2%, M^+), 219 (100, M − Me), 189 (49, M − 3 × Me) and 143 (83, M − 4-MeC_6H_4) (Found: M^+, 234.1084. $C_{13}H_{18}O_2Si$ requires *M*, 234.1076).

Dimethyl (3*RS*,4*SR*)-3,4-bis[dimethyl(4-methylphenyl)silyl]-hexane-1,6-dioate 8b

Freshly prepared samarium diiodide[26] (0.09 mol dm^{-3} in THF, 180 cm^3) was added to the acrylate **7** (3.51 g, 15 mmol) and dimethyl malonate (6 g, 45.5 mmol) in dry DMPU (30 cm^3) under nitrogen over 25 min at room temperature. After 1 min, the mixture was quenched with aqueous sodium hydrogen carbonate (saturated, 400 cm^3) and extracted with ether (3 × 200 cm^3). The extracts were washed with water and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was kept in methanol (120 cm^3) overnight, and the crystals collected to give the *diester* (1.55 g, 44%). The filtrate was evaporated under reduced pressure, and the residue was chromatographed (SiO_2, EtOAc–hexane, 15:85) to give a second crop (1.01 g, 28%, 72% overall), mp 96–97 °C (from MeOH); R_f(EtOAc–hexane, 1:9) 0.2; ν_{max}($CHCl_3$)/cm^{-1} 1735 (C=O), 1260 (SiMe) and 1110 (Si–Ar); δ_H(250 MHz; $CDCl_3$) 7.32 (4 H, d, *J* 7.8, Ar), 7.14 (4 H, d, *J* 7.8, Ar), 3.50 (6 H, s, 2 × OMe), 2.45 (2 H, dd, *J* 7.5 and 16.4, 2 × C$H_AH_B$$CO_2$Me), 2.34 (2 H, dd, *J* 5.9 and 16.4, 2 × C$H_AH_B$$CO_2$Me), 2.33 (6 H, s, 2 × 4-*Me*C_6H_4), 1.84–1.76 (2 H, m, 2 × SiCH), 0.26 (6 H, s, 2 × SiMe) and 0.21 (6 H, s, 2 × SiMe); *m*/*z* 455 (79%, M − Me), 439 (23, M − OMe), 397 (80, M − CH_2CO_2Me), 321 (47, M − 4-$MeC_6H_4SiMe_2$) and 149 (100, 4-$MeC_6H_4SiMe_2$) (Found: C, 66.27; H, 8.19. $C_{26}H_{38}O_4Si_2$ requires C, 66.33; H, 8.14%), and *methyl dimethyl*(4-*methylphenyl*)*silylpropanoate* **10b** (840 mg, 24%); R_f(EtOAc–hexane, 5:95) 0.37; ν_{max}(film)/cm^{-1} 1750 (C=O), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.38 (2 H, d, *J* 7.8, Ar), 7.17 (2 H, d, *J* 7.8, Ar), 3.61 (3 H, s, OMe), 2.34 (3 H, s, 4-*Me*C_6H_4), 2.30–2.23 (2 H, m, CH_2CO_2Me), 1.1–1.02 (2 H, m, $SiCH_2$) and 0.26 (6 H, s, $SiMe_2$); *m*/*z* 236 (0.2%, M^+), 221 (100, M − Me), 205 (12, M − OMe), 149 (59, 4-$MeC_6H_4Me_2Si$) and 145 (70, M − 4-MeC_6H_4) (Found: M^+, 236.1227. $C_{13}H_{20}O_2Si$ requires *M*, 236.1232).

Mixture of dimethyl (3*RS*,4*SR*)-3,4-bis[dimethyl(4-methylphenyl)silyl]hexane-1,6-dioate 8b and dimethyl (3*RS*,4*RS*)-3,4-bis[dimethyl(4-methylphenyl)silyl]hexane-1,6-dioate 9b

Following the method of Inanaga,[4] freshly prepared samarium diiodide (0.1 mol dm^{-3} in THF, 100 cm^3) was added to the (*E*)-acrylate **5b** (2.55 g, 10 mmol based on unsaturated ester present) and *tert*-butyl alcohol (740 mg, 10 mmol) in dry hexamethylphosphoric triamide (20 cm^3) under nitrogen over 25 min at room temperature. After 1 min, the mixture was quenched with aqueous sodium hydrogen carbonate (saturated, 400 cm^3) and extracted with ether (3 × 200 cm^3). The extracts were washed with water and brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 15:85) to give the *meso* diester **8b** (1.26 g, 54%), *racemic diester* **9b** (265 mg, 11%); R_f(EtOAc–hexane, 1:9) 0.26; ν_{max}(film)/cm^{-1} 1745 (C=O), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.34 (4 H, d, *J* 7.8, Ar), 7.12 (4 H, d, *J* 7.8, Ar), 3.44 (6 H, s, 2 × OMe), 2.32 (6 H, s, 4-*Me*C_6H_4), 2.17 (2 H, dd, *J* 10.1 and 15.9, 2 × C$H_AH_B$$CO_2$Me), 2.07 (2 H, dd, *J* 3.8 and 15.9, 2 × C$H_AH_B$$CO_2$Me), 1.75 (2 H, dd, *J* 3.8 and 10.1, 2 × SiCH), 0.24 (6 H, s, 2 × SiMe) and 0.22 (6 H, s, 2 × SiMe); *m*/*z* 455 (10%, M − Me), 397 (13, M − CH_2CO_2Me), 321 (14, M − 4-$MeC_6H_4Me_2Si$) and 149 (100, 4-$MeC_6H_4Me_2Si$) (Found: C, 66.22; H, 8.16; M − Me, 455.2081. $C_{26}H_{38}O_4Si_2$ requires C, 66.33; H, 8.14%; *M* − Me, 455.2074), and the propanoate **10b** (703 mg, 30%).

Dimethyl (3*RS*,4*SR*)-3,4-bis[dimethyl(phenyl)silyl]hexane-1,6-dioate 8a and dimethyl (3*RS*,4*RS*)-3,4-bis[dimethyl(phenyl)-silyl]hexane-1,6-dioate 9a

Similarly, the (*E*)-acrylate **5a**[6] (630 mg, 2 mmol of unsaturated ester) gave after chromatography (SiO_2, EtOAc–hexane, 7:93) the meso *diester* **8a** (210 mg, 48%), mp 41–42 °C (from hexane); R_f(EtOAc–hexane, 5:95) 0.23; ν_{max}(film)/cm^{-1} 1740 (C=O), 1260 (SiMe) and 1120 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.46–7.37 (4 H, m, Ph), 7.34–7.28 (6 H, m, Ph), 3.50 (6 H, s, 2 × OMe), 2.47 (2 H, dd, *J* 7.4 and 16.5, 2 × C$H_AH_B$$CO_2$Me), 2.38 (2 H, dd, *J* 6.2 and 16.5, 2 × C$H_AH_B$$CO_2$Me), 1.88–1.80 (2 H, m, 2 × SiCH), 0.28 (6 H, s, 2 × SiMe) and 0.23 (6 H, s, 2 × SiMe);

m/*z* 427 (25.5%, M − Me) and 135 (100, $PhMe_2Si$) (Found: C, 65.06; H, 7.78 $C_{24}H_{34}O_4Si_2$ requires C, 65.11; H, 7.74), *racemic diester* **9a** (74 mg, 17%), R_f(EtOAc–hexane, 5:95) 0.29; ν_{max}(film)/cm^{-1} 1740 (C=O), 1250 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.47–7.43 (4 H, m, Ph), 7.36–7.27 (6 H, m, Ph), 3.43 (6 H, s, 2 × OMe), 2.19 (2 H, dd, *J* 10.1 and 16, 2 × CH_AH$_B$CO$_2$Me), 2.07 (2 H, dd, *J* 3.6 and 16, 2 × CH$_A$$H_BCO_2$Me), 1.77 (2 H, dd, *J* 3.6 and 10.1, 2 × SiCH), 0.26 (6 H, s, 2 × SiMe) and 0.24 (6 H, s, 2 × SiMe); *m*/*z* 427 (5.8%, M − Me) and 135 (62.7, $PhMe_2Si$) and 84 (100) (Found: C, 65.29; H, 7.81. $C_{24}H_{34}O_4Si_2$ requires C, 65.11; H, 7.74%), and methyl dimethyl(phenyl)silylpropanoate[27] (110 mg, 25% allowing for that in the starting material); R_f(EtOAc–hexane, 5:95) 0.38; ν_{max}(film)/cm^{-1} 1740 (C=O), 1250 (SiMe) and 1120 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.51–7.45 (2 H, m, Ph), 7.38–7.32 (3 H, m, Ph), 3.61 (3 H, s, OMe), 2.31–2.22 (2 H, m, CH_2CO$_2$Me), 1.16–1.04 (2 H, m, SiCH$_2$) and 0.28 (6 H, s, $SiMe_2$).

(2*RS*,3*RS*,4*SR*)-2-Methoxycarbonyl-3,4-bis[dimethyl(4-methylphenyl)silyl]cyclopentan-1-one

Method A. *n*-Butyllithium (1.5 mol dm^{-3} in hexane, 0.4 cm^3) was added dropwise to diisopropylamine (0.1 cm^3, 0.65 mmol) in dry THF (2 cm^3) under nitrogen at −78 °C. After 20 min at 0 °C, the mixture was brought back to −78 °C and the diester **8b** (235 mg, 0.5 mmol) in dry THF (2 cm^3) was added dropwise over 15 min. The mixture was stirred at −78 °C for 6 h, quenched at 0 °C with hydrochloric acid (3 mol dm^{-3}) and extracted with ether (3 × 20 cm^3). The extract was washed with aqueous sodium hydrogen carbonate and with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *keto ester* (200 mg, 91%); R_f(EtOAc–hexane, 15:85) 0.31; ν_{max}(film)/cm^{-1} 1760 (C=O), 1735 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.31–7.26 (4 H, m, Ar), 7.13 (4 H, d, *J* 7.8, Ar), 3.51 (3 H, s, OMe), 3.11 (1 H, d, *J* 8.0, CHCO), 2.50–2.26 (3 H, m, CH_2 and SiCH), 2.34 (6 H, s, 4-*Me*C$_6$H$_4$), 2.23–2.08 (1 H, m, SiCH), 0.25 (3 H, s, SiMe), 0.24 (3 H, s, SiMe), 0.23 (3 H, s, SiMe) and 0.22 (3 H, s, SiMe); *m*/*z* 438 (0.7%, M$^+$), 379 (5.7, M − COOMe) and 149 (100, 4 − MeC$_6$HMe$_2$Si) (Found: M$^+$, 438.2056. $C_{25}H_{34}O_3Si_2$ requires *M*, 438.2046).

Method B. Freshly prepared samarium diiodide (0.09 mol dm^{-3} in THF, 230 cm^3) was added with mechanical stirring to the (*E*)-acrylate **5b** (5.1 g, 20 mmol of unsaturated ester) in dry DMPU (40 cm^3) under nitrogen at room temperature over 20–25 min, and stirred for 30 min. *tert*-Butyl alcohol (1.85 g, 25 mmol) in dry THF (50 cm^3) was added dropwise over 1 h, and the mixture kept for 2 h at room temperature. The mixture was quenched and worked up as before, with chromatography (SiO_2, EtOAc–hexane, 10:90) to give the *keto ester* (3.11 g, 70%) contaminated with the *meso* diester **8b** (8:2, by integration of the signals at δ 3.50 and 3.11) Partial removal of the diester **8b** by crystallisation from methanol was possible.

(2*RS*,3*RS*,4*RS*)-2-Methoxycarbonyl-3,4-bis[dimethyl(4-methylphenyl)silyl]cyclopentan-1-one

Similarly, using method A, the diester **9b** (235 mg, 0.5 mmol) gave, after chromatography (SiO_2, EtOAc–hexane, 1:9), the *keto ester* (143 mg, 65%) as a mixture of tautomers (keto:enol, ~6:4); R_f(EtOAc–hexane, 15:85) 0.47; ν_{max}($CDCl_3$)/cm^{-1} 3400 (OH), 1750 (C=O), 1730 (C=O), 1660 (C=C), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 10.35 (1 H, s, OH-enol), 7.33–7.28 (8 H, m, Ar), 7.17–7.09 (8 H, m, Ar), 3.57 (3 H, s, OMe-enol), 3.52 (3 H, s, OMe-keto), 3.11 (1 H, d, *J* 10.6, CHCO-keto), 2.34 (6 H, s, 2 × 4-*Me*C$_6$H$_4$), 2.33 (6 H, s, 2 × 4-*Me*C$_6$H$_4$), 2.54–2.12 (6 H, m, 2 × CH_2 and 2 × SiCH), 1.60–1.40 (2 H, m, 2 × SiCH), 0.21 (6 H, s, 2 × SiMe-enol), 0.18 (9 H, s, SiMe-keto and 2 × SiMe-enol), 0.16 (3 H, s, SiMe-keto), 0.13 (3 H, s, SiMe-keto) and 0.11 (3 H, s, SiMe-keto); *m*/*z* 438 (4.0%, M$^+$), 423 (5.3, M − Me) and 149 (100, 4-MeC$_6$H$_4$SiMe$_2$) (Found: M$^+$, 438.2081. $C_{25}H_{34}O_3Si_2$ requires *M*, 438.2046).

(3*RS*,4*SR*)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopentan-1-one 11

Following the method of Krapcho and Lovey,[28] the keto ester prepared from **8b** (2.19 g, 5 mmol), sodium chloride (590 mg, 10 mmol), water (0.2 cm^3, 11 mmol) and dimethyl sulfoxide (20 cm^3) were heated under nitrogen at 130–150 °C for 3 h. The mixture was poured into water and extracted with ether (3 × 40 cm^3). The extracts were washed with water and with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *ketone* (1.635 g, 86%) as cubes, mp 80–81 °C (from hexane); R_f(EtOAc–hexane, 1:9) 0.42; ν_{max}($CHCl_3$)/cm^{-1} 1745 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.29 (4 H, d, *J* 7.7, Ar), 7.12 (4 H, d, *J* 7.7, Ar), 2.34 (6 H, s, 2 × 4-*Me*C$_6$H$_4$), 2.29 (2 H, dd, *J* 9.4 and 18.6, 2 × CH_AH$_B$CO), 2.14 (2 H, dd, *J* 7.3 and 18.6, 2 × CH$_A$$H_B$CO), 2.04–1.92 (2 H, m, 2 × SiCH) and 0.24 (12 H, s, 2 × $SiMe_2$); *m*/*z* 380 (2.6%, M$^+$) and 149 (100, 4-MeC$_6$H$_4$SiMe$_2$) (Found: C, 72.80; H, 8.59; M$^+$, 380.1957. $C_{23}H_{32}OSi_2$ requires C, 72.57; H, 8.47%; *M*, 380.1991).

(3*RS*,4*RS*)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopentan-1-one 14

Similarly, (2*RS*,3*RS*,4*RS*)-2-methoxycarbonyl-3,4-bis[dimethyl(4-methylphenyl)silyl]cyclopentanone (44 mg, 0.1 mmol) gave the *ketone* (30 mg, 78%); R_f(EtOAc–hexane, 1:9) 0.24; ν_{max}($CDCl_3$)/cm^{-1} 1740 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.32 (4 H, d, *J* 7.8, Ar), 7.15 (4 H, d, *J* 7.8, Ar), 2.34 (6 H, s, 2 × 4-*Me*C$_6$H$_4$), 2.09 (4 H, d, *J* 7.4, 2 × CH_2CO), 1.61 (2 H, t, *J* 7.4, 2 × SiCH), 0.21 (6 H, s, 2 × SiMe) and 0.20 (6 H, s, 2 × SiMe); *m*/*z* 380 (11.2%, M$^+$), 365 (1.4, M − Me) and 149 (100, 4-MeC$_6$H$_4$-$SiMe_2$) (Found: M$^+$, 380.1961. $C_{23}H_{32}OSi_2$ requires *M*, 380.1991).

(1α,3α,4α)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopentan-1-ol

Sodium borohydride (3 mg, 0.08 mmol) and the ketone **11** (28 mg, 0.074 mmol) were stirred in propan-2-ol (1 cm^3) at 0 °C for 1.5 h and at room temperature for 1 h. The solvent was removed under reduced pressure. The residue was acidified with hydrochloric acid and extracted with ether (2 × 5 cm^3). The extract was washed with aqueous sodium hydrogen carbonate and with brine, dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (26 mg, 92%); R_f(EtOAc–hexane, 2:8) 0.33; ν_{max}($CDCl_3$)/cm^{-1} 3630 (OH), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.32 (4 H, d, *J* 7.8, Ar), 7.11 (4 H, d, *J* 7.8, Ar), 4.31–4.20 (1 H, m, C*H*OH), 2.33 (6 H, s, 2 × 4-*Me*C$_6$H$_4$), 2.16–2.05 (2 H, m, 2 × SiCH), 1.63–1.40 (4 H, m, 2 × CH_2), 0.24 (6 H, s, 2 × SiMe) and 0.19 (6 H, s, 2 × SiMe) (Found: C, 71.99; H, 8.78. $C_{23}H_{34}OSi_2$ requires C, 72.18; H, 8.95%).

(1β,3β,4α)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopentan-1-ol

Similarly, the ketone **14** (15 mg, 0.04 mmol) in ethanol (1 cm^3) gave the *alcohol* (14 mg, 94%); R_f(EtOAc–hexane, 2:8) 0.33; ν_{max}($CHCl_3$)/cm^{-1} 3380 (OH), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.37 (2 H, d, *J* 7.8, Ar), 7.34 (2 H, d, *J* 7.8, Ar), 7.15 (4 H, d, *J* 7.8, Ar), 3.96 (1 H, quintet, *J* 6.1, C*H*OH), 2.34 (6 H, s, 2 × 4-*Me*C$_6$H$_4$), 2.00–1.89 (1 H, m, SiCH), 1.82–1.73 (1 H, m, SiCH), 1.61–1.17 (4 H, m, 2 × CH_2), 0.18 (3 H, s, SiMe), 0.17 (3 H, s, SiMe), 0.14 (3 H, s, SiMe) and 0.13 (3 H, s, SiMe) (Found: C, 72.09; H, 8.90. $C_{23}H_{34}OSi_2$ requires C, 72.18; H, 8.95%).

(1α,3α,4α)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopent-1-yl acetate 12

Acetic anhydride (0.01 cm^3, 0.1 mmol), the (1α,3α,4α)-alcohol (8 mg, 0.02 mmol) and 4-dimethylaminopyridine (1.2 mg, 0.01 mmol) were kept in pyridine (0.2 cm^3) at room temperature for 15 h. Water (3 cm^3) was added and the mixture was extracted with ether (2 × 5 cm^3). The extract was washed with aqueous copper sulfate and with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) to give the *acetate* (8 mg, 90%); R_f(EtOAc–hexane, 1:9) 0.30; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.30 (4 H, d, *J* 7.7, Ar), 7.11 (4 H, d, *J* 7.7, Ar), 5.14–4.94 (1 H, m, C*H*OAc), 2.33 (6 H, s, 2 × 4-*Me*C_6H_4), 2.30–2.06 (2 H, m, 2 × SiCH), 2.02 (3 H, s, OAc), 1.62–1.50 (4 H, m, 2 × CH_2), 0.22 (6 H, s, 2 × SiMe) and 0.19 (6 H, s, 2 × SiMe); *m*/*z* 409 (1.5%, M − Me) and 149 (100, 4-Me$C_6H_4SiMe_2$) (Found: C, 70.89; H, 8.60. $C_{25}H_{36}O_2Si_2$ requires C, 70.69; H, 8.54%). The acetate was contaminated with 7–8% of its diastereoisomer **13** as judged by the OAc peak at δ 1.93.

(1β,3α,4α)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopent-1-yl acetate 13

Diethyl azodicarboxylate (DEAD)[9] (17.4 mg, 0.1 mmol) in ether (0.2 cm^3), the (1β,3α,4α)-alcohol (30 mg, 0.078 mmol), triphenylphosphine (27 mg, 0.1 mmol) and acetic acid (0.006 cm^3, 0.1 mmol) were stirred in ether (0.3 cm^3) under argon at room temperature for 5 h. Hexane (2 cm^3) was added and the mixture filtered. The filtrate was evaporated under reduced pressure and the residue was purified by preparative thin layer chromatography (SiO_2, EtOAc–hexane, 1:9) to give the *acetate* (26 mg, 78%); R_f(EtOAc–hexane, 1:9) 0.30; ν_{max}(film)/cm^{-1} 1730 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.30 (4 H, d, *J* 7.8, Ar), 7.11 (4 H, d, *J* 7.8, Ar), 5.17–5.04 (1 H, m, C*H*OAc), 2.33 (6 H, s, 2 × 4-*Me*C_6H_4), 2.10–1.91 (1 H, m, SiCH), 1.93 (3 H, s, OAc), 1.86–1.74 (3 H, m, CH_2 and SiCH), 0.19 (6 H, s, 2 × SiMe) and 0.17 (6 H, s, 2 × SiMe); *m*/*z* 424 (0.2%, M^+), 409 (1.2, M − Me), 149 (100, 4-MeC_6H_4-$SiMe_2$) (Found: C, 70.23; H, 8.52; M^+, 424.2267. $C_{25}H_{36}O_2Si_2$ requires C, 70.69; H, 8.54%; *M*, 424.2253). The acetate was contaminated with 7–8% of its diastereoisomer **12** as judged by the OAc peak at δ 2.02.

(1β,3β,4α)-3,4-Bis[dimethyl(4-methylphenyl)silyl]cyclopent-1-yl acetate 15

Similarly, the (1β,3β,4α)-alcohol (20 mg, 0.05 mmol) gave the *acetate* (19 mg, 86%); R_f(EtOAc–hexane, 1:9) 0.33; ν_{max}-$(CDCl_3)/cm^{-1}$ 1735 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.35 (2 H, d, *J* 7.8, Ar), 7.34 (2 H, d, *J* 7.8, Ar), 7.14 (4 H, d, *J* 7.8, Ar), 4.90 (1 H, quintet, *J* 6.1, C*H*OAc), 2.34 (6 H, s, 2 × 4-*Me*C_6H_4), 2.03 (1 H, ddd, *J* 6.4, 9.4 and 13.2, SiCH), 1.95 (3 H, s, OAc), 1.86 (1 H, ddd, *J* 6.4, 6.4 and 13.2, SiCH), 1.70 (1 H, ddd, *J* 6.1, 9.4 and 13.2, CH_AH_B-CHO), 1.60–1.24 (3 H, m, CH_AH_BCHO and CH_2), 0.18 (3 H, s, SiMe), 0.15 (3 H, s, SiMe), 0.14 (3 H, s, SiMe) and 0.11 (3 H, s, SiMe); *m*/*z* 424 (0.1%, M^+) and 149 (100, 4-Me$C_6H_4SiMe_2$) (Found: C, 70.81; H, 8.49; M^+, 424.2268. $C_{25}H_{36}O_2Si_2$ requires C, 70.69; H, 8.54%; *M*, 424.2253). The same compound (10 mg, 75%) was prepared from the (1β,3β,4α)-alcohol (12 mg, 0.031 mmol) following the method for preparation of (1β,3α,4α)-3,4-bis[dimethyl(4-methylphenyl)silyl]cyclopent-1-yl acetate **13**.

(3*RS*,4*SR*)-3,4-Bis[dimethyl(4-methylphenyl)silyl]pentan-5-olide 16

m-Chloroperoxybenzoic acid (50% w/w, 2.1 g, 6 mmol) in dichloromethane (10 cm^3) was dried ($MgSO_4$) and then stirred with the ketone **11** (1.14 g, 3 mmol) and disodium hydrogen orthophosphate (3.5 g, 25 mmol) in dichloromethane (15 cm^3) at room temperature for 5 h. The mixture was filtered and diluted with ether (100 cm^3). The filtrate was washed with aqueous sodium thiosulfate and with aqueous sodium hydrogen carbonate, dried (K_2CO_3) and evaporated under reduced pressure to give the *lactone* (1.2 g, 99%) as cubes, mp 87–88 °C (from MeOH); R_f(EtOAc–hexane, 2:8) 0.25; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.31 (2 H, d, *J* 7.8, Ar), 7.27 (2 H, d, *J* 7.8, Ar), 7.16 (2 H, d, *J* 7.8, Ar), 7.14 (2 H, d, *J* 7.8, Ar), 4.39 (2 H, d, *J* 6.0, CH_2OCO), 2.64 (1 H, dd, *J* 7.3 and 18.5, CH_AH_BCO), 2.57 (1 H, dd, *J* 7 and 18.5, CH_AH_BCO), 2.36 (3 H, s, 4-*Me*C_6H_4), 2.35 (3 H, s, 4-*Me*C_6H_4), 1.75–1.58 (2 H, m, 2 × SiCH), 0.31 (3 H, s, SiMe), 0.29 (3 H, s, SiMe) and 0.28 (6 H, s, 2 × SiMe); *m*/*z* 396 (45.8%, M^+) and 149 (100, 4-Me$C_6H_4SiMe_2$) (Found: C, 69.70; H, 8.22; M^+, 396.1944. $C_{23}H_{32}O_2Si_2$ requires C, 69.64; H, 8.13%; *M*, 396.1941). This reaction was also carried out without the orthophosphate, when the ketone **11** (0.5 mmol) and *m*-chloroperoxybenzoic acid (1.5 mmol) in dichloromethane at room temperature for 15 h gave the same *lactone* (185 mg, 95%).

(3*RS*,4*RS*)-3,4-Bis[dimethyl(4-methylphenyl)silyl]pentan-5-olide 22

Similarly, the ketone **14** (0.38 g, 1 mmol) gave the *lactone* (300 mg, 75%) as needles, mp 95–96 °C (from hexane); R_f(EtOAc–hexane, 2:8) 0.28; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O), 1610 (Ar), 1260 (SiMe) and 1110 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.36 (2 H, d, *J* 7.8, Ar), 7.35 (2 H, d, *J* 7.8, Ar), 7.19 (4 H, d, *J* 7.8, Ar), 4.10 (1 H, dd, *J* 5.5 and 11.5, CH_AH_BOCO), 4.0 (1 H, dd, *J* 4.5 and 11.5, CH_AH_BOCO), 2.4–2.33 (2 H, m, CH_2CO), 2.35 (6 H, s, 2 × 4-*Me*C_6H_4), 1.48–1.36 (2 H, m, 2 × SiCH), 0.27 (3 H, s, SiMe), 0.22 (3 H, s, SiMe), 0.18 (3 H, s, SiMe) and 0.17 (3 H, s, SiMe); *m*/*z* 396 (25.7%, M^+) and 149 (100, 4-Me$C_6H_4SiMe_2$) (Found: C, 69.76; H, 8.09; M^+, 396.1942. $C_{23}H_{32}O_2Si_2$ requires C, 69.64; H, 8.13%; *M*, 396.1941).

2-Deoxyribonolactone

Peracetic acid (32–36% w/v in AcOH, 5 cm^3) was stirred with the lactone **16** (400 mg, 1 mmol), potassium bromide (285 mg, 2.4 mmol) and sodium acetate (1 g, 12.2 mmol) in acetic acid (5 cm^3) at room temperature for 15 h. The solvent was azeotropically removed with toluene under vacuum. The residue was triturated with MeOH–EtOAc (1:99), filtered and the filtrate was evaporated under reduced pressure. IR spectra and TLC showed that the product was a mixture of γ-lactone [R_f(MeOH–EtOAc, 1:99) 0.26; $\nu_{max}(CHCl_3)/cm^{-1}$ 1770] and δ-lactone [R_f(MeOH–EtOAc, 1:99) 0.18; $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 cm^{-1}]. The residue was kept in methanol (2 cm^3) and hydrochloric acid (3 mol dm^{-3} in H_2O, 1 cm^3) for 48 h. The solvent was removed under vacuum and the residue was chromatographed (SiO_2, MeOH–EtOAc, 1:99) to give the γ-lactone[29] (76 mg, 58%); R_f(MeOH–EtOAc, 1:99) 0.26; ν_{max}(film)/cm^{-1} 3400 (OH), 1770 (C=O); δ_H(250 MHz, D_2O) 4.58–4.50 (2 H, m, C*H*OH and CHOCO), 3.86 (1 H, dd, *J* 2.9 and 13.0, CH_AH_BOH), 3.75 (1 H, dd, *J* 4.3 and 13.0, CH_AH_B-OH), 3.04 (1 H, dd, *J* 6.8 and 18.5, CH_AH_BCO) and 2.57 (1 H, dd, *J* 2.9 and 18.5, CH_AH_BCO); *m*/*z* 133 (1.5%, M^+ + H), 101 (72, M − CH_2OH) and 44 (100, CO_2) (Found: M^+ + H, 133.0506. $C_5H_9O_4$ requires *M* + H, 133.0500).

(3*RS*,4*SR*)-3,5-Diacetoxypentan-1,4-olide 18

Acetic anhydride (0.2 cm^3 containing 1% v/v of 70% perchloric acid) was stirred with the diol (20 mg, 0.15 mmol) at room temperature for 0.5 h. The mixture was diluted with ice cold water and extracted with dichloromethane (3 × 5 cm^3). The extract was washed with aqueous sodium hydrogen carbonate and with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:1) to give the diacetate[13] (25 mg, 76%); R_f(EtOAc–hexane, 1:1) 0.29; ν_{max}(film)/cm^{-1} 1790 (C=O) and 1740 (C=O); δ_H(250 MHz, $CDCl_3$) 5.26 (1 H, ddd, *J* 1.8, 1.8 and 7.4, C*H*OAc), 4.67 (1 H, ddd, *J* 1.8, 3.5 and 3.5, CHOCO), 4.37

(1 H, dd, *J* 3.5 and 12.4, C*H*$_A$H$_B$OAc), 4.26 (1 H, dd, *J* 3.5 and 12.4, CH$_A$*H*$_B$OAc), 2.99 (1 H, dd, *J* 7.4 and 18.7, C*H*$_A$H$_B$CO), 2.61 (1 H, dd, *J* 1.8 and 18.7, CH$_A$*H*$_B$CO), 2.10 (3 H, s, OAc) and 2.08 (3 H, s, OAc); *m*/*z* 217 (94%, M$^+$ + H), 143 (97, M − CH$_2$OAc), 128 (65, M − CH$_2$OAc + Me), 83 (100, M − CH$_2$OAc + AcOH) (Found: M$^+$ + H, 217.0693. $C_9H_{13}O_6$ requires *M* + H, 217.0712).

(2*RS*,3*SR*,4*RS*)-3,4-Bis[dimethyl(4-methylphenyl)silyl]-2-hydroxypentan-5-olide

Following Davis,[30] the lactone **16** (2.39 g, 6 mmol) in THF (10 cm^3) was added to a stirred solution of sodium hexamethyldisilazide (1 mol dm^{-3} in THF, 10 cm^3) in dry THF (10 cm^3) under nitrogen at −78 °C. After 30 min at −78 °C, 2-phenylsulfonyl-3-phenyloxaziridine[31] (3.13 g, 12 mmol) in dry THF (12 cm^3) was added dropwise over 10 min and the mixture was stirred for 30 min. Camphorsulfonic acid (2.52 g, 10 mmol) in dry THF (10 cm^3) was added to the mixture, followed by saturated aqueous ammonium chloride at −78 °C, and the mixture extracted with ethyl acetate (3 × 100 cm^3). The extract was washed with 5% aqueous citric acid and with aqueous sodium hydrogen carbonate, dried (MgSO$_4$) and evaporated under reduced pressure. The residue was left for 2 days to allow the sulfonylimine to decompose to sulfonamide and benzaldehyde, and chromatographed (SiO$_2$, EtOAc–hexane, 15:85) to give the *lactone* (1.73 g, 70%); R_f(EtOAc–hexane, 15:85) 0.16; ν_{max}(CDCl$_3$)/cm^{-1} 3440 (OH), 1720 (C=O), 1600 (Ar), 1250 (SiMe) and 1110 (SiAr); δ_H(250 MHz; CDCl$_3$) 7.37 (2 H, d, *J* 7.9, Ar), 7.18–7.10 (6 H, m, Ar), 4.40 (2 H, d, *J* 4.6, CH$_2$OCO), 4.27 (1 H, dd, *J* 1.5 and 9.3, C*H*OH), 2.97 (1 H, d, *J* 1.5, OH), 2.37 (3 H, s, 4-*Me*C$_6$H$_4$), 2.34 (3 H, s, 4-*Me*C$_6$H$_4$), 1.92–1.80 (2 H, m, 2 × SiCH), 0.35 (3 H, s, SiMe), 0.33 (3 H, s, SiMe), 0.26 (3 H, s, SiMe) and 0.23 (3 H, s, SiMe); *m*/*z* 395 (3%, M − OH), 149 (100, 4-MeC$_6$H$_4$SiMe$_2$) and 91 (38, 4-MeC$_6$H$_4$) (Found: M$^+$ − OH, 395.1841. $C_{23}H_{31}O_2Si_2$ requires *M* − OH, 395.1862).

(2*RS*,3*SR*,4*RS*)-2-*tert*-Butyldimethylsilyloxy-3,4-bis[dimethyl-(4-methylphenyl)silyl]pentan-5-olide 19

The hydroxylactone (412 mg, 1 mmol), imidazole (360 mg, 5 mmol) and *tert*-butylchlorodimethylsilane (375 mg, 2.5 mmol) in dry DMF (1.5 cm^3) were stirred at room temperature for 15 h. The mixture was poured into water and extracted with ether (3 × 25 cm^3). The extract was washed with aqueous sodium hydrogen carbonate and with brine, dried (MgSO$_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, EtOAc–hexane, 1:9) to give the *silyl ether* (490 mg, 93%) as needles, mp 93–94 °C (from hexane); R_f(EtOAc–hexane, 1:9) 0.29; ν_{max}(CHCl$_3$)/cm^{-1} 1740 (C=O), 1610 (Ar), 1260 (SiMe), 1110 (SiAr) and 1040 (SiO); δ_H(250 MHz; CDCl$_3$) 7.32 (2 H, d, *J* 7.9, Ar), 7.21 (2 H, d, *J* 7.9, Ar), 7.18 (2 H, d, *J* 7.9, Ar), 7.13 (2 H, d, *J* 7.9, Ar), 4.41 (1 H, ddd, *J* 1.5, 5.3 and 11.4, C*H*$_A$H$_B$OCO), 4.31 (1 H, dd, *J* 11.4 and 13.6, CH$_A$*H*$_B$OCO), 4.15 (1 H, d, *J* 1.5, CHOSi), 2.68 (1 H, ddd, *J* 3, 5.3 and 13.6, SiCH), 2.37 (3 H, s, 4-*Me*C$_6$H$_4$), 2.33 (3 H, s, 4-*Me*C$_6$H$_4$), 1.55 (1 H, ddd, *J* 1.5, 1.5 and 3, SiCH), 0.85 (9 H, s, SiBu^t), 0.3 (3 H, s, SiMe), 0.29 (3 H, s, SiMe), 0.25 (3 H, s, SiMe), 0.23 (3 H, s, SiMe), −0.02 (3 H, s, SiMe) and −0.11 (3 H, s, SiMe); *m*/*z* 526 (1.3%, M$^+$), 511 (1.8, M − Me), 469 (1.8, M − Bu^t), 435 (1.7, M − 4-MeC$_6$H$_4$), 395 (2, M − OSiMe$_2$Bu^t) and 149 (100, 4-MeC$_6$H$_4$SiMe$_2$) (Found: C, 66.18; H, 8.93; M$^+$, 526.2766. $C_{29}H_{46}O_3Si_3$ requires C, 66.10; H, 8.80%; *M*, 526.2755).

(2*SR*,3*RS*,4*RS*)-2-*tert*-Butyldimethylsilyloxy-3,5-dihydroxy-valero-1,4-lactone 20

Peracetic acid (32–36% w/v in AcOH, 36 cm^3), potassium bromide (1.144 g, 9.6 mmol) and sodium acetate (10 g, 122 mmol) were stirred with the lactone **19** (2.104 g, 4 mmol) in acetic acid (25 cm^3) at room temperature for 15 h. The solvent was azeotropically removed with toluene at room temperature under vacuum. The residue was taken up in ethyl acetate (100 cm^3), filtered and the filtrate was evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, EtOAc–hexane, 7:3) to give the *lactone* (670 mg, 64%) as needles, mp 107–108 °C (from hexane); R_f(EtOAc–hexane, 1:1) 0.21; ν_{max}(CH$_2$Cl$_2$)/cm^{-1} 3600 (OH), 1800 (C=O) and 840 (SiO); δ_H(250 MHz, CDCl$_3$) 4.45–4.35 (2 H, m, CHOSi and CHOCO), 4.19–4.08 (1 H, m, CHOH), 3.98 (1 H, dd, *J* 3 and 12.8, C*H*$_A$H$_B$OH), 3.81 (1 H, dd, *J* 3.6 and 12.8, CH$_A$*H*$_B$OH), 0.93 (9 H, s, SiBu^t), 0.16 (3 H, s, SiMe) and 0.10 (3 H, s, SiMe); *m*/*z* 263 (0.6%, M + H), 205 (53, M − Bu^t) and 75 (100, SiMe$_2$OH) (Found: M$^+$ + H, 263.1322. $C_{11}H_{23}O_5Si$ requires *M* + H, 263.1315).

(±)-Tri-*O*-acetylarabono-1,4-lactone 21

Tetrabutylammonium fluoride (1 mol dm^{-3} in THF, 0.8 cm^3) was stirred with the lactone **20** (96 mg, 0.37 mmol) in dry THF (1 cm^3) under nitrogen at room temperature for 30 min. The solvent was evaporated off, and the residue was taken up in EtOAc–MeOH (95:5), filtered through silica gel (8 cm) and the filtrate was evaporated under reduced pressure. The residue was treated with acetic anhydride (1 cm^3, containing 1% v/v of 70% perchloric acid) and stirred at room temperature for 30 min. The mixture was poured onto crushed ice, stirred for 30 min and extracted with dichloromethane (3 × 10 cm^3). The extract was washed with water and with brine, dried (MgSO$_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO$_2$, EtOAc–hexane, 8:2) to give the triacetate[12] (71 mg, 71%); R_f(EtOAc) 0.58; ν_{max}(CH$_2$Cl$_2$)/cm^{-1} 1800 (C=O, lactone) and 1750 (C=O, acetate); δ_H(250 MHz, CDCl$_3$) 5.57 (1 H, d, *J* 7, OCOC*H*OAc), 5.46 (1 H, dd, *J* 7 and 7, C*H*OAc), 4.55 (1 H, ddd, *J* 3, 4.8 and 7, CHOCO), 4.48 (1 H, dd, *J* 3 and 12.5, C*H*$_A$CH$_B$OAc), 4.29 (1 H, dd, *J* 4.8 and 12.5, CH$_A$*H*$_B$OAc), 2.19 (3 H, s, OAc), 2.13 (3 H, s, OAc) and 2.12 (3 H, s, OAc); δ_C(100 MHz, CDCl$_3$) 170.27, 169.84, 169.47, 168.24, 77.39, 72.54, 72.17, 62.05, 20.57, 20.53 and 20.35; *m*/*z* 275 (3.2%, M + H), 274 (1.1, M$^+$), 232 (29, M − CH$_2$CO), 214 (19, M − AcOH), 201 (32, M − CH$_2$OAc), 154 (80, M − 2 × AcOH), 128 (96, M − 2 × CH$_2$OAc) and 115 (100) (Found: M$^+$, 274.0683. $C_{11}H_{14}O_8$ requires *M*, 274.0689).

2-Deoxyxylonolactone diacetate 24

Similarly to the preparation of the lactone **18** from the lactone **16**, the lactone **22** (60 mg, 0.15 mmol) was converted to the diol lactone **23** (13.5 mg, 68%), which was treated with aqueous methanolic hydrochloric acid (1 mol dm^{-3} in MeOH–H$_2$O, 2:1, 6 cm^3) for 48 h at room temperature, worked up and chromatographed (SiO$_2$, EtOAc–hexane, 4:6) to give the diacetate[13] (16 mg, 73%) (50% overall); R_f(EtOAc–hexane, 1:1) 0.20; ν_{max}(CHCl$_3$)/cm^{-1} 1790 (C=O) and 1740 (C=O); δ_H(250 MHz, CDCl$_3$) 5.55 (1 H, ddd, *J* 2.3, 4.9 and 7.0, C*H*OCO), 4.77 (1 H, q, *J* 5, CHOAc), 4.38–4.28 (2 H, m, CH$_2$OAc), 2.91 (1 H, dd, *J* 6.5 and 18.2, C*H*$_A$H$_B$CO), 2.62 (1 H, dd, *J* 2.3 and 18.2, CH$_A$*H*$_B$CO), 2.10 (3 H, s, OAc) and 2.09 (3 H, s, OAc).

(3*RS*,4*SR*)-3,5-Bis[dimethyl(4-methylphenyl)silyl]pentan-1,4-olide 30

Potassium hydroxide (0.1 mol dm^{-3} in MeOH–H$_2$O, 9:1, 75 cm^3) and the lactone **16** (2 g, 5 mmol) were stirred in methanol (5 cm^3) at room temperature for 2 h. The solvent was removed under reduced pressure and the residue was acidified with aqueous citric acid, extracted with dichloromethane (2 × 25 cm^3) and dried (MgSO$_4$). A sample from an earlier run was concentrated to identify the hydroxy acid **28**; R_f(EtOAc–hexane, 3:7) 0.17; ν_{max}(CHCl$_3$)/cm^{-1} 3400–2500 (br, OH and COOH), 1700 (C=O), 1600 (Ar), 1260 (SiMe) and 1100 (SiAr); δ_H(250 MHz; CDCl$_3$) 7.37 (4 H, d, *J* 7.8, Ar), 7.16 (2 H, d, *J* 7.8, Ar), 7.13 (2 H, d, *J* 7.8, Ar), 3.73 (1 H, dd, *J* 4.9 and 11.2, C*H*$_A$H$_B$OH), 3.67 (1 H, dd, *J* 7.2 and 11.2, CH$_A$*H*$_B$OH), 2.57 (1 H, dd, *J* 8.6 and 17.2, C*H*$_A$H$_B$CO), 2.44 (1 H, dd, *J* 4.9 and 17.2, CH$_A$*H*$_B$CO), 2.33 (3 H, s, 4-*Me*C$_6$H$_4$), 2.32 (3 H, s,

4-*Me*C_6H_4), 1.84 (1 H, ddd, *J* 4.9. 4.9 and 8.6, SiCH), 1.47 (1 H, ddd, *J* 4.9, 4.9 and 7.2, SiCH), 0.29 (3 H, s, SiMe), 0.28 (3 H, s, SiMe), 0.25 (3 H, s, SiMe) and 0.24 (3 H, s, SiMe). Triphenylphosphine (1.835 g, 7 mmol) was added, the mixture was cooled to −20 °C and DEAD (1.22 g, 7 mmol) was added with stirring under nitrogen at −20 °C. After 2.5 h at room temperature, the solvent was removed under reduced pressure and the residue was triturated with ether–hexane (1:1), filtered and the filtrate was concentrated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 15:85) to give the *lactone* (1.4 g, 70%) as needles, mp 79–80 °C (from MeOH); R_f(EtOAc–hexane, 15:85) 0.37; ν_{max}($CHCl_3$)/cm^{-1} 1760 (C=O), 1600 (Ar), 1250 (SiMe) and 1105 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.32 (2 H, d, *J* 7.8, Ar), 7.23 (2 H, d, *J* 7.8, Ar), 7.18 (2 H, d, *J* 7.8, Ar), 7.15 (2 H, d, *J* 7.8, Ar), 4.38 (1 H, ddd, *J* 4.5, 9 and 9.8, CHOCO), 2.47 (1 H, dd, *J* 9 and 17.5, CH_AH_BCO), 2.37 (3 H, s, 4-*Me*C_6H_4), 2.36 (3 H, s, 4-*Me*C_6H_4), 2.26 (1 H, dd, *J* 12.5 and 17.5, CH$_A$$H_B$CO), 1.57 (1 H, ddd, *J* 9.9 and 12.5, SiCH), 1.09–0.93 (2 H, m, $SiCH_2$), 0.30 (3 H, s, SiMe) and 0.28 (9 H, s, $SiMe_2$ and SiMe); *m*/*z* 396 (2%, M^+) and 149 (100, 4-Me$C_6H_4SiMe_2$) (Found: C, 69.70; H, 8.30; M^+, 396.1942. $C_{23}H_{32}O_2Si_2$ requires C, 69.64; H, 8.13%; *M*, 396.1941), and the lactone **16** (275 mg, 14%). The reaction was monitored by IR, no absorption at around 1820 cm^{-1} for an intermediate β-lactone was observed.

(3*RS*,4*RS*)-3,5-Bis[dimethyl(4-methylphenyl)silyl]valero-1,4-lactone 27

Similarly, the lactone **22** (130 mg, 0.33 mmol) in methanol (2 cm^3) with potassium hydroxide (0.5 mol dm^{-3} in MeOH–THF–water, 8:1:14 cm^3) was converted to a solution of the hydroxy acid **31**, which was treated with triphenylphosphine (173 mg, 0.66 mmol) and DEAD (116 mg, 0.66 mmol), worked up and chromatographed (SiO_2, Et_2O–hexane, 30:70) to give the *lactone* (92 mg, 71%) as needles, mp 109–110 °C (from MeOH); R_f(Et_2O–hexane, 30:70) 0.25; ν_{max}($CHCl_3$)/cm^{-1} 1760 (C=O), 1600 (Ar), 1250 (SiMe) and 1100 (SiAr); δ_H(250 MHz; $CDCl_3$) 7.35 (2 H, d, *J* 7.8, Ar), 7.27 (2 H, d, *J* 7.8, Ar), 7.18 (2 H, d, *J* 7.8, Ar), 7.14 (2 H, d, *J* 7.8, Ar), 4.74 (1 H, ddd, *J* 2.8, 7.2 and 10, CHOCO), 2.51 (1 H, dd, *J* 12.8 and 17.2, CH_AH_BCO), 2.42 (1 H, dd, *J* 3.6 and 17.2, CH$_A$$H_B$CO), 2.37 (3 H, s, 4-*Me*C_6H_4), 2.34 (3 H, s, 4-*Me*C_6H_4), 2.19–2.07 (1 H, m, SiCH), 1.05 (1 H, dd, *J* 10 and 14.5, SiCH_AH_B), 0.90 (1 H, dd, *J* 2.8 and 14.5, SiCH$_A$$H_B$), 0.35 (3 H, s, SiMe), 0.32 (3 H, s, SiMe), 0.29 (3 H, s, SiMe) and 0.24 (3 H, s, SiMe); *m*/*z* 396 (32.3%, M^+) and 149 (100, 4-Me$C_6H_4SiMe_2$) (Found: C, 69.65; H, 8.20; M^+, 396.1934. $C_{23}H_{32}O_2Si_2$ requires C, 69.64; H, 8.13%; *M*, 396.1941), and recovered lactone **22** (20 mg, 15%).

2-Deoxyribonolactone from the lactone 30

The lactone **30** (400 mg, 1 mmol) was converted to deoxyribonolactone (78 mg, 59%), identical (TLC, IR, ^{1}H NMR) with the earlier sample, using potassium bromide (300 mg, 2.4 mmol), sodium acetate (3 g, 36.6 mmol) and peracetic acid (10 cm^3, of a 32% w/v solution in acetic acid) in acetic acid (16 cm^3) following the method for its preparation from the δ-lactone **16**, except that no acid treatment was needed to change lactone ring size.

(3*RS*,4*SR*)-2-Deoxyribonolactone diacetate [(3*RS*,4*SR*)-3,5-diacetoxypentan-1,4-olide] 18

Acetic anhydride (0.2 cm^3, containing 1% w/v of 70% perchloric acid) was stirred with the lactone (20 mg, 0.15 mmol) at room temperature for 0.5 h, and worked up as before to give the diacetate (27 mg, 83%), identical (TLC, IR, ^{1}H NMR) with the earlier sample.

2-Deoxyxylonolactone diacetate 24

Similar to the preparation of the lactone **18** from the lactone **30**, the lactone **27** (60 mg, 0.15 mmol) gave successively 2-deoxyxylonolactone and its diacetate (14 mg, 44% overall) identical (TLC, IR, ^{1}H NMR) with the earlier sample.

Reaction of (3*RS*,4*SR*)-3,4-bis[dimethyl(4-methylphenyl)silyl-pentan-5-olide 16 with camphorsulfonic acid

The lactone **16** (40 mg, 0.1 mmol) was stirred with camphorsulfonic acid (4 mg, 0.016 mmol) in dichloromethane (2 cm^3) at room temperature for 4 days. The solvent was removed under reduced pressure and the residue was purified by preparative layer chromatography (SiO_2, EtOAc–hexane, 3:7) to give mainly 5-[dimethyl(4-methylphenyl)silyl]pent-3-enoic acid (15 mg, 60%) (*E*:*Z*, 45:55); R_f(EtOAc–hexane, 30:70) 0.24; δ_H(250 MHz, $CDCl_3$) 7.39 (2 H, d, *J* 7.8, Ar), 7.38 (2 H, d, *J* 7.8, Ar), 7.16 (4 H, d, *J* 7.8, Ar), 5.70–5.30 (4 H, m, CH=CH), 3.02 (2 H, d, *J* 6.6, CH_2CO of *E*), 2.97 (2 H, d, *J* 7.1, CH_2CO of *Z*), 2.33 (6 H, s, 4-*Me*C_6H_4), 1.70 (4 H, d, *J* 8.2, $SiCH_2$), 0.26 (6 H, s, $SiMe_2$ of *Z*) and 0.24 (6 H, s, $SiMe_2$ of *E*), and recovered lactone **16** (10 mg, 25%). The mixture of acids was treated with ethereal diazomethane to give the mixture of esters; R_f(EtOAc–hexane, 10:90) 0.39; GC (SGE BP-5, 0.32 mm id, 25 m, film thickness 0.25 micron; 200 °C isothermal) **35** (44%, t_R = 5.08 min), **37** (52%, t_R = 5.36 min) and **36** (4%, t_R = 4.35 min); ν_{max}(film)/cm^{-1} 1730 (C=O), 1600 (Ar), 1250 (SiMe) and 1100 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.38 (2 H, d, *J* 7.9, Ar), 7.37 (2 H, d, *J* 7.9, Ar), 7.16 (4 H, d, *J* 7.9, Ar), 5.70–5.330 (4 H, m, CH=CH), 3.66 (3 H, s, OMe, *E*), 3.65 (3 H, s, OMe, *Z*), 2.99 (2 H, d, *J* 6.5, CH_2CO, *E*), 2.94 (2 H, d, *J* 6.8, CH_2CO, *Z*), 2.34 (6 H, s, 4-*Me*C_6H_4), 1.68 (4 H, d, *J* 7.8, $SiCH_2$), 0.25 (6 H, s, $SiMe_2$, *Z*), 0.24 (6 H, s, $SiMe_2$, *E*).

Reactions of lactones with boron trifluoride–diethyl ether

Typically, boron trifluoride–diethyl ether (1.6×10^{-3} cm^3, 0.013 mmol) was kept with the lactone (50 mg, 0.125 mmol) in dichloromethane (1 cm^3) under nitrogen at room temperature for 1–3 days. The solvent was evaporated under reduced pressure, the residue was esterified with ethereal diazomethane, purified by preparative layer chromatography (SiO_2, EtOAc–hexane, 10:90) and analysed by GC (details above). The following lactones were treated in this way.

The lactone 16 gave after 3 days the lactone **16** (10%) and a mixture of esters (80%) in the ratios **35**:**37**:**36** 49:37:14.

The lactone 30 gave after 40 h the mixture of esters (85%) in the ratios **35**:**37**:**36** 76:5:19.

The lactone 27 gave after 28 h the mixture of esters (93%) in the ratios **35**:**37**:**36** 4:90:6. Data for *methyl* (Z)-5-*dimethyl*(4-*methylphenyl*)*silylpent*-3-*enoate* **37** δ_H(250 MHz, $CDCl_3$) 7.39 (2 H, d, *J* 7.9, Ar), 7.16 (2 H, d, *J* 7.9, Ar), 5.60 (1 H, ttd, *J* 1.5, 7.0 and 10.5, CH=C*H*CH_2CO), 5.45 (1 H, ttd, *J* 0.8, 8.3 and 10.5, CH=C*H*CH_2Si), 3.65 (3 H, s, OMe), 2.94 (2 H, dd, *J* 1.5 and 7.0, CH_2CO), 2.34 (3 H, s, 4-*Me*C_6H_4), 1.69 (2 H, dd, *J* 0.8 and 8.3, $SiCH_2$) and 0.26 (6 H, s, $SiMe_2$).

Reactions of lactones with tetrabutylammonium fluoride

Typically, tetrabutylammonium fluoride (1 mol dm^{-3} in THF, 0.4 cm^3) was stirred with the lactone (80 mg, 0.2 mmol) in dry THF (1 cm^3) at room temperature for 0.5–1.5 h. Methyl iodide (0.1 cm^3, 1.6 mmol) was added and the mixture was stirred for 15 min, poured into water and extracted with ether (2×10 cm^3). The extract was washed with water and with brine, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was chromatographed (SiO_2, EtOAc–hexane, 1:9) and analysed by GC (details above). The following lactones were treated in this way.

The lactone 16 gave after 30 min *methyl* 3-*dimethyl*(4-*methylphenyl*)*silylpent*-4-*enoate* **36** (94%) isomerically pure; R_f(EtOAc–hexane, 10:90) 0.39; ν_{max}(film)/cm^{-1} 1735 (C=O), 1620 (C=C), 1600 (Ar), 1250 (SiMe) and 1100 (SiAr); δ_H(250 MHz, $CDCl_3$) 7.37 (2 H, d, *J* 7.8, Ar), 7.17 (2 H, d, *J* 7.8, Ar), 5.70 (1 H, ddd, *J* 7.5, 10.5 and 17.3, C*H*=CH_2), 4.90 (1 H, d, *J* 10.5, CH=CH_AH_B), 4.81 (1 H, d, *J* 17.3, CH=CH$_A$$H_B$), 3.58 (3 H, s,

OMe), 2.46–2.23 (3 H, m, SiCH and CH_2CO), 2.34 (3 H, s, 4-*Me*C_6H_4), 0.27 (3 H, s, SiMe) and 0.26 (3 H, s, SiMe); *m*/*z* 262 (52.5%, M^+) and 149 (100, 4-$MeC_6H_4SiMe_2$) (Found: C, 68.83; H, 8.63; M^+, 262.1371. $C_{15}H_{22}O_2Si$ requires C, 68.65; H, 8.45%; *M*, 262.1389).

The lactone 30 gave after 1 h the mixture of esters (92%) in the ratios **35**:**37**:**36** 60:1:39. Data for *methyl* (E)-5-*dimethyl*(4-*methylphenyl*)*silylpent*-3-*enoate* **35** δ_H(250 MHz, $CDCl_3$) 7.39 (2 H, d, *J* 7.9, Ar), 7.17 (2 H, d, *J* 7.9, Ar), 5.53 (1 H, td, *J* 7.8 and 15.6, CH=C*H*CH_2CO), 5.34 (1 H, td, *J* 7.0 and 15.6, CH=C*H*CH_2Si), 3.66 (3 H, s, OMe), 2.98 (2 H, d, *J* 7.8, CH_2CO), 2.34 (3 H, s, 4-*Me*C_6H_4), 1.69 (2 H, d, *J* 7.0, $SiCH_2$) and 0.24 (6 H, s, $SiMe_2$) (Found: C, 68.55; H, 8.30; M, 262.1375. $C_{15}H_{22}O_2Si$ requires C, 68.65; H, 8.45%; *M*, 262.1389).

The lactone 27 gave after 1.5 h the mixture of esters (83%) in the ratios **35**:**37**:**36** 8:41:51.

Acknowledgements

We thank the Commission of the European Communities for a grant, B/CII*-913098, to S. K. G., and Professor Albert Eschenmoser for a stimulating correspondence about the mechanism of the rearrangement **28** ⟶ **30**.

References

1 A. Barbero, D. C. Blakemore, I. Fleming and R. N. Wesley, *J. Chem. Soc.*, *Perkin Trans. 1*, 1997, 1329.
2 M. Ahmar, C. Duyck and I. Fleming, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 2721.
3 I. Fleming and S. K. Ghosh, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1775 and 1777.
4 J. Inanaga, Y. Handa, T. Tabuchi, K. Otsubo, M. Yamaguchi and T. Hanamoto *Tetrahedron Lett.*, 1991, **32**, 6557.
5 A. Cabrera and H. Alper, *Tetrahedron Lett.*, 1992, **33**, 5007.
6 K. Takeshita, Y. Seki, K. Kawamoto, S. Murai and N. Sonoda, *J. Org. Chem.*, 1987, **52**, 4864.
7 N. Abd.Rahman, I. Fleming and A. B. Zwicky, *J. Chem. Res.* (*S*), 1992, 292; *J. Chem. Res.* (*M*), 1992, 2401.
8 A. P. Krapcho, *Synthesis*, 1982, 805.
9 O. Mitsunobu, *Synthesis*, 1981, 1.
10 I. Fleming, R. Henning, D. C. Parker, H. E. Plaut and P. E. J. Sanderson, *J. Chem. Soc.*, *Perkin Trans. 1*, 1995, 317.
11 F. A. Davis and A. C. Sheppard, *Tetrahedron*, 1989, **45**, 5703.
12 K. Bock, I. Lundt and C. Pedersen, *Acta Chem. Scand.*, *Sect. B*, 1981, **35**, 155.
13 B. Rague, Y. Chapleur and B. Castro, *J. Chem. Soc.*, *Perkin Trans. 1*, 1982, 2063.
14 B. J. Pradhan, PhD Thesis, Cambridge, 1996.
15 R. P. C. Cousins and N. S. Simpkins, *Tetrahedron Lett.*, 1989, **30**, 7241; C. M. Cain, R. P. C. Cousins, G. Coumbarides and N. S. Simpkins, *Tetrahedron*, 1990, **46**, 523; P. J. Cox and N. S. Simpkins, *Synlett*, 1991, 321.
16 P. F. Hudrlik, A. M. Hudrlik, G. Nagendrappa, T. Yimenu, E. T. Zellers and E. Chin, *J. Am. Chem. Soc.*, 1980, **102**, 6894 with a correction *J. Am. Chem. Soc.*, 1982, **104**, 1157; P. F. Hudrlik, A. M. Hudrlik, T. Yimenu, M. A. Waugh and G. Nagendrappa, *Tetrahedron*, 1988, **44**, 3791.
17 G. Procter, A. T. Russell, P. J. Murphy, T. S. Tan and A. N. Mather, *Tetrahedron*, 1988, **44**, 3953.
18 M. T. Reetz, *Angew. Chem.*, *Int. Ed. Engl.*, 1972, **11**, 129.
19 B. Capon and S. P. McManus, *Neighbouring Group Participation*, Vol. 1, Plenum, New York, 1976.
20 M. Suginome, A. Takama and Y. Ito, *J. Am. Chem. Soc.*, 1998, **120**, 1930.
21 I. Fleming, *Chemtracts*, *Org. Chem.*, 1993, **6**, 113; J. B. Lambert, *J. Organomet. Chem.*, 1996, **521**, 203; J. B. Lambert and Y. Zhao, *J. Am. Chem. Soc.*, 1996, **118**, 7867.
22 J. E. Baldwin, *J. Chem. Soc.*, *Chem. Commun.*, 1976, 734.
23 N. Shimizu, S. Imazu, F. Shibata and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 1122.
24 D. W. Lewis and G. C. Gainer, *J. Am. Chem. Soc.*, 1952, **74**, 2931.
25 G. Solladié and C. Hamdouchi, *Synthesis*, 1991, 979.
26 T. Imamoto and M. Ono, *Chem. Lett.*, 1987, 501.
27 I. Ojima and M. Kumagai, *J. Organomet. Chem.* 1976, **111**, 43.
28 A. P. Krapcho and A. J. Lovey, *Tetrahedron Lett.*, 1973, 957.
29 Y. Kita, O. Tamura, F. Itoh, H. Yasuda, H. Kishino, Y. Y. Ke and Y. Tamura, *J. Org. Chem.*, 1988, **53**, 554.
30 F. A. Davis, L. C. Vishwakarma, J. M. Billmers and J. Finn, *J. Org. Chem.*, 1984, **49**, 3241.
31 F. A. Davis, J. Lamendola Jr., U. Nadir, E. W. Kluger, T. C. Sedergran, T. W. Panunto, R. E. Billmers, R. Jenkins Jr., I. J. Turchi, W. H. Watson, J. S. Chen and M. Kimura, *J. Am. Chem. Soc.*, 1980, **102**, 2000; R. Albrecht, G. Kresze and B. Malkar, *Chem. Ber.*, 1964, **97**, 483; F. A. Davis and O. D. Stringer, *J. Org. Chem.*, 1982, **47**, 1774.

Paper 8/04282I
Received 5*th June* 1998
Accepted 25*th June* 1998