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EPOXY-SILANES IN ORGANIC SYNTHESIS

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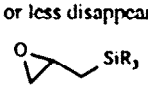
Abstract *Stereoselective reactions involving functionalised β,γ-epoxysilanes and epoxide-allylsilanes provide a range of synthetically useful transformations.*

The reactivity of epoxy-silanes depends upon the regiochemical relationship between the epoxide group and the silyl substituent, and upon the nature of the silane unit itself. α,β-Epoxysilanes (1) undergo a number of synthetically useful reactions including rearrangement to carbonyl compounds and ring opening with nucleophiles.[1] Placing a methylene group between the silyl substituent and the epoxide group of (1) produces β,γ-epoxysilanes (2) and results in a dramatic change in reactivity. Now the chemistry is dominated by the ease of elimination of (2) to produce allylic alcohols,[2] a reaction with significant synthetic potential. Both of these types of epoxy-silane are useful in a general synthetic sense, but as the epoxide group becomes more remote from the silyl substituent (γ,δ-epoxysilanes and above) (3), the special reactivity due to the proximity of the two groups more or less disappears, and the synthetic value drops rapidly.


(1)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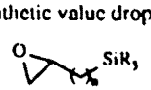

(3) n ≥ 2

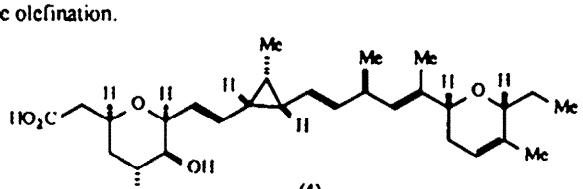
Systems in which the epoxide is remote from the silyl substituent become interesting from a synthetic point of view when this substituent is present as an allylsilane since the possibility of cyclisation of the allylsilane onto the epoxide arises, a reaction which could be of use for the synthesis of carbocycles or heterocycles (reaction *1*).[3]


1

Herein we describe some of our recent work on the use of reactions which involve chiral β,γ-epoxysilanes for the stereoselective synthesis of potentially useful synthetic units, and on the cyclisation of some simple epoxide allylsilanes (Reaction *1*).

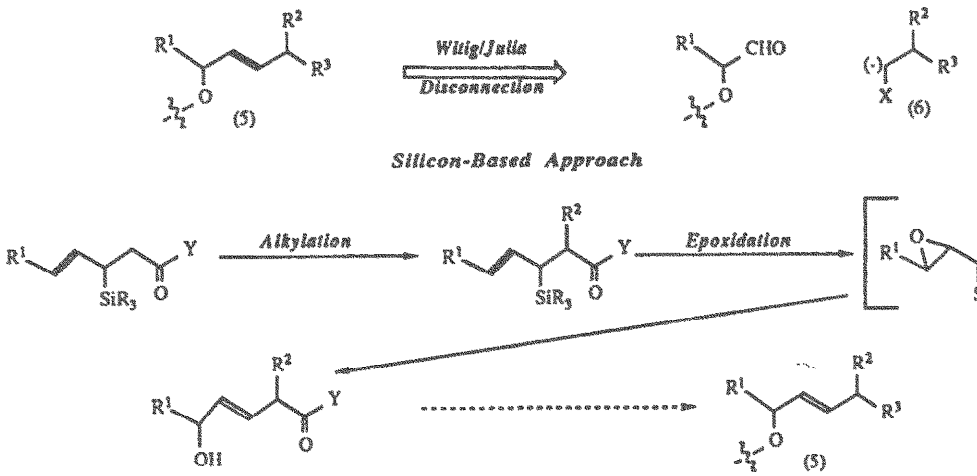
Stereoselective reactions of β,γ-epoxysilanes generated by the oxidation of chiral acyclic allylsilanes

As a result of work in our laboratories (in collaboration with Dr. A.H. Davidson, UWIST)[4] on a convergent total synthesis the antifungal antibiotic ambruticin (4), it became apparent to us that olefinic systems with the general structure (5) were particularly difficult to prepare by the "obvious" approach of coupling the two chiral fragments using reactions such as Wittig or Julia type olefination.


(4)

In our experience when the nucleophilic species is moderately hindered [e.g. β-branching in (6)] and the aldehyde is both β-branched and highly enolisable, this direct coupling approach can be very difficult indeed. An alternative approach to systems such as (5) is outlined in Scheme 1, and utilises a silyl substituent to control the relative and absolute stereochemistry of the chiral centres in (5).

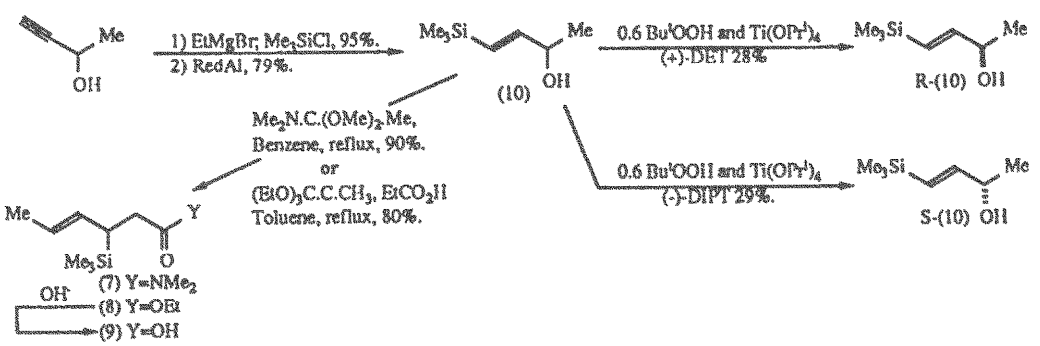
Scheme 1



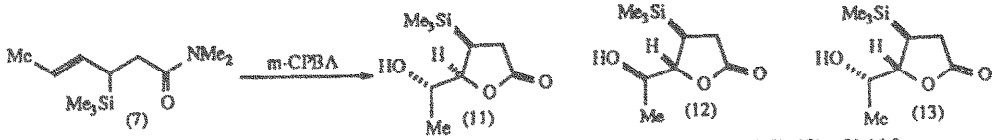
For this silicon-based approach to be of any value, a number of stereochemical issues must be resolved. Given that the alkylation step is likely to be stereoselective, as shown by Fleming *et al.*,[5] the epoxidation/elimination sequence then becomes critically important, since it is in this sequence that the relative stereochemistry of the hydroxyl group and R^2 is established. Furthermore, the double bond is formed in the elimination step of this sequence, and it is important that this takes place with good stereoselectivity. Previous work by Kumada *et al.*[6] and Fleming *et al.*[7], and reports which appeared during our initial investigations confirm that the desired stereochemical control in the epoxidation/elimination sequence is possible.

Our initial investigations centered upon the chemistry of the amide-allylsilanes[8] and the ester-allylsilanes[9] (Scheme 1, Y=NMe_2 and Y=OEt respectively). The allylsilanes (7), (8) and (9) were readily prepared using the appropriate version of the Claisen rearrangement[10,11] as shown in Scheme 2, and the racemic allylic alcohol (10) proved to be an excellent substrate for Sharpless kinetic resolution.[8,12]

Scheme 2



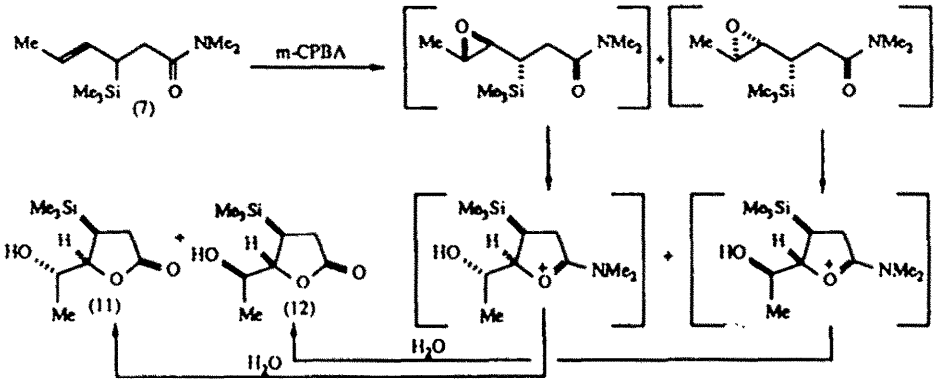
In addition to the racemate, both enantiomers of the amide-allylsilane (7) were prepared and their reaction with *meta*-chloroperoxybenzoic acid (m-CPBA) was studied. We were surprised to find that none of the expected allylic alcohol was formed in this reaction, the products were shown (*vide infra*) to be the isomeric γ-lactones (11), (12), and (13).



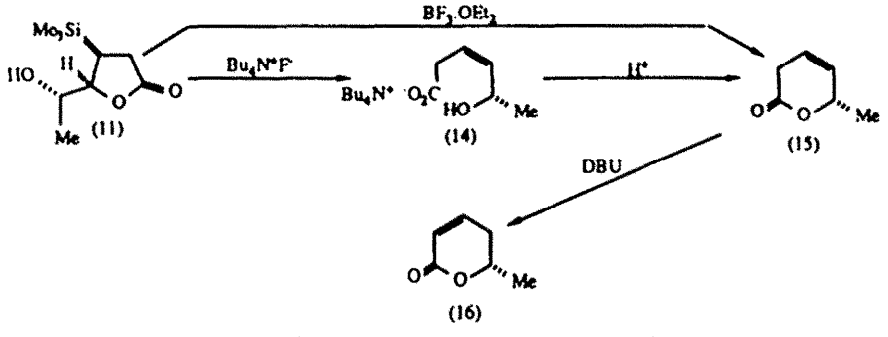
Combined yield ~ 75%, (11):(12):(13) ≈ 81:16:3

Presumably the γ-lactones (11) and (12) arise from epoxidation of either face of the double bond and intramolecular nucleophilic attack of the amide carbonyl group on the epoxide (which must be more rapid than elimination to the allylic alcohol), followed by hydrolysis of the resulting iminium ion. The formation of small quantities of γ-lactone (13) was puzzling at this stage, but became clear in the light of further experiments on the ester-allylsilanes (*vide infra*). A plausible mechanism for the formation of γ-lactones (11) and (12) is outlined in Scheme 3.

Scheme 3

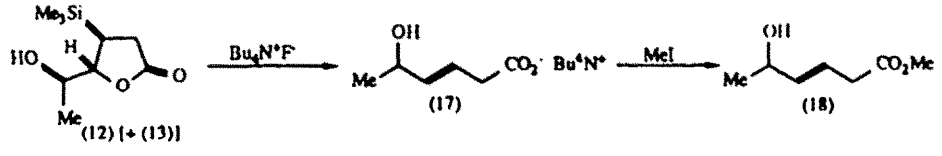


The unexpected formation of these γ-lactones was fortunate since it replaced the amide group, which is rather difficult to manipulate, with the reactive and synthetically versatile lactone group and this allowed us to carry out further synthetic transformations under mild conditions. Moreover the major γ-lactone (11) was easy to isolate and crystalline making this material attractive for further synthetic studies. We discovered that treatment of γ-lactone (11) with tetra-n-butylammonium fluoride (TBAF)[13] in tetrahydrofuran (THF) followed by removal of the solvent gave the *cis*-salt (14) in essentially quantitative yield, and on acidification the deconjugated δ-lactone (15) was isolated. This δ-lactone was produced directly in very high yield on treatment of (14) with boron trifluoride etherate ($BF_3.OEt_2$). No trace (^1H nmr) of the conjugated δ-



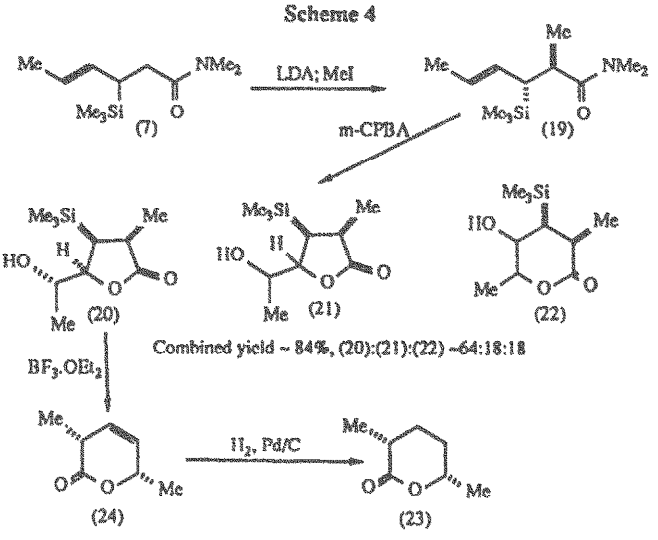
lactone (16) could be detected in the product from either of these reactions. This conjugated δ-lactone (15), parasorbic acid,[14] was easily prepared by treatment with 1,8-diazabicyclo[4,5,0]-7-undecene (DBU). The conversion of optically active samples of the γ-lactone (11) derived from S-(10) into the naturally occurring antipode of parasorbic acid [that shown in structure (16)] determined the absolute configuration of the hydroxyl-bearing carbon of (11) to be as shown. In addition this finding made it very likely that the other two chiral centres of (11) were as shown, since the chirality at the carbon carrying the silyl substituent was established as S- by the Eschenmoser-Claisen rearrangement,[10] and the stereochemical realtionship between this centre and the adjacent centre follows from the formation of the *cis*-alkene on elimination.[13]

As expected, treatment of the γ-lactone (12) [contaminated with a small quantity of (13)] gave the corresponding *trans*-salt (17) which was converted into the ester (18) in high yield (this has only been carried out in the racemic series so far).



With the epoxidation/elimination sequence worked out for the amide-allylsilane (7) we then investigated the alkylation of this amide and the effect of the alkyl group on the oxidative lactonisation. As expected[5] the alkylation was highly stereoselective producing effectively a single diastereoisomer (19) as shown (Scheme 4). Treatment of this alkylated amide-allylsilane with m-CPBA again gave a mixture of lactones as shown. The major product isolated in 53% yield by chromatography was shown to be the γ-lactone (20) by X-ray crystallography.[15] This lactone was converted into the carpenter bee pheromone (23)[16] by elimination with $BF_3.OEt_2$ followed by hydrogenation of the double bond as shown below.

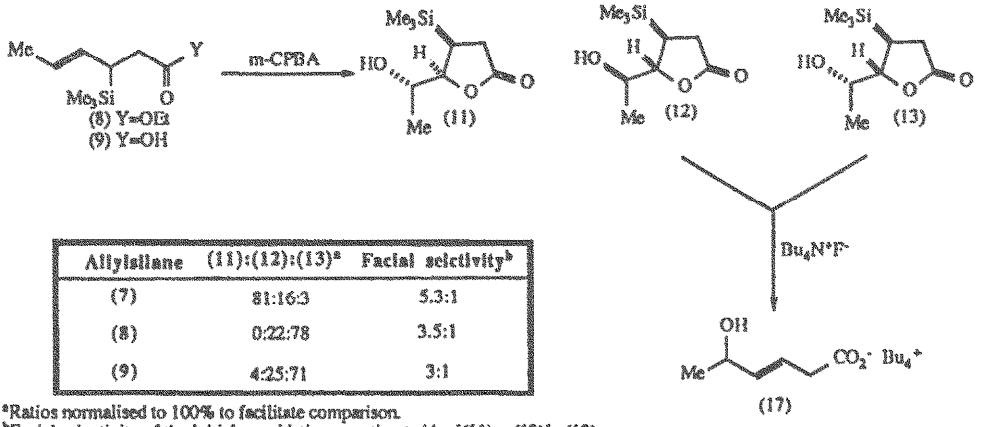
Scheme 4



Although the formation of the deconjugated γ-lactone (24) was expected from our earlier result with the amide allylsilane (7),nevertheless it is most interesting since it should be possible to functionalise the double bond in the γ-lactone (24) without conjugation occurring.

With these results in hand we turned our attention to the reaction of the corresponding ester-allylsilane (8) and the acid-allylsilane (9) with m-CPBA. Once again γ-lactones were formed but to our surprise the ratio of the stereoisomers was completely different from that obtained with the amide-allylsilane (7). The γ-lactone (13) was now the major product, whereas in the case of the amide-allylsilane (7) this isomer was formed in very small amounts, for comparison the relevant ratios are given in the table in Scheme 5.

Scheme 5



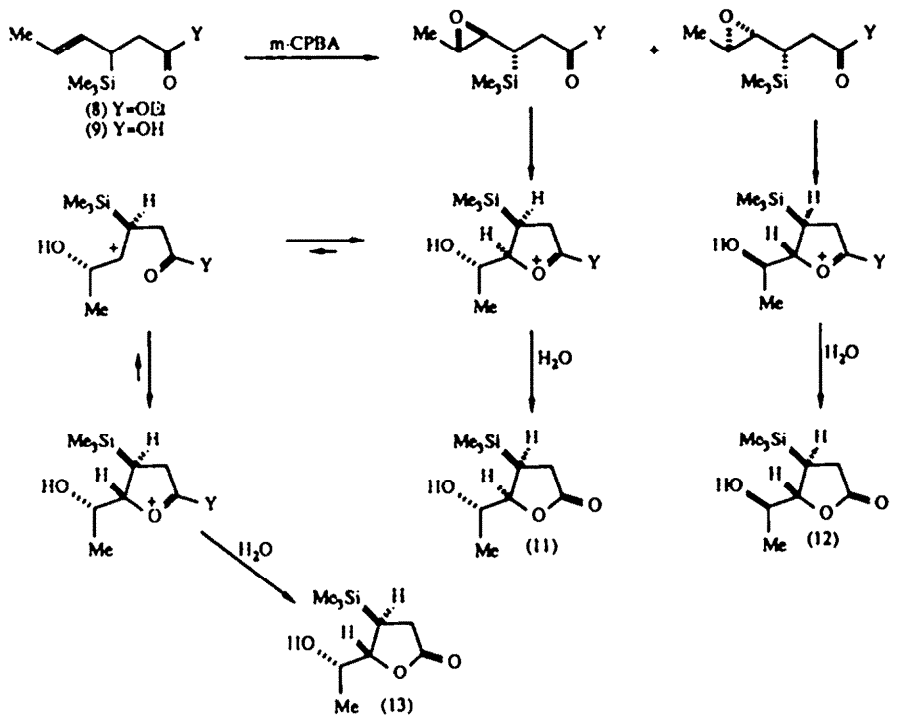
Allylsilane	(11):(12):(13)[a]	Facial selectivity[b]
(7)	81:16:3	5.3:1
(8)	0:22:78	3.5:1
(9)	4:25:71	3:1

[a]Ratios normalised to 100% to facilitate comparison.
[b]Facial selectivity of the initial epoxidation as estimated by [(11) + (13)] : (12).

It is possible that this change in product distribution is due to equilibration of the oxonium ion (Schemes 3 and 6) derived from the major epoxide. Initially this ion has the adjacent trimethylsilyl substituent and the hydroxy-ethyl group *cis*-, whereas in the equilibrated ion these bulky groups are *trans*-, which is presumably the more stable arrangement. A

possible sequence for this is outlined in Scheme 6. The oxonium ions derived from the ester and acid are likely to be intrinsically less stable than that derived from the amide and therefore more easily equilibrated (the "open" carbonium ion is presumed to be of similar stability in all these cases). There would be little driving force for the oxonium ion derived from the minor epoxide to equilibrate since the *trans*- isomer is formed directly.

Scheme 6



The observation that much more equilibration occurs with the alkylated amide (19) than with amide (7) is consistent with this picture since the oxonium ion which would be produced initially from the major epoxide would be less stable than that from (7) as it possesses three *cis*-ring substituents.

Irrespective of the mechanistic detail, we believe that the work which is outlined here could be of use in organic synthesis since it does offer the prospect of stereochemical control and control of double bond geometry using a common strategy. Clearly much more work remains to be carried out in this area and we are actively pursuing the development of the methodology and investigating some synthetic applications of this chemistry.

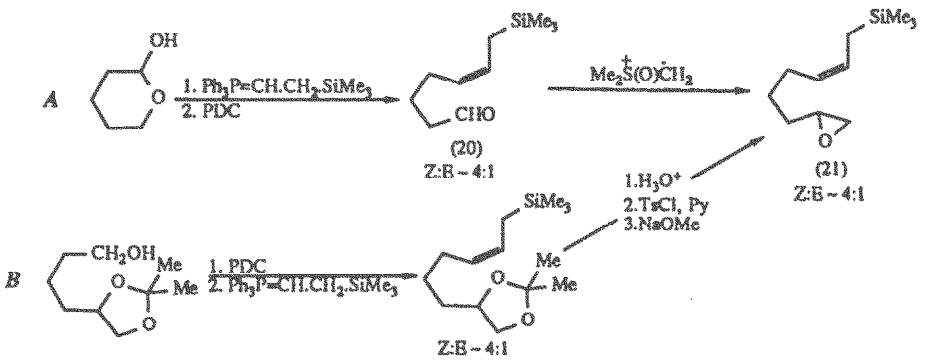
Cyclisations of epoxide-allylsilanes

Cyclisations of allyl and vinyl silanes on to electrophilic centres with the simultaneous formation of a new C-C bond have been known for some time,[17] indeed this type of cyclisation has been used as an important part of several total syntheses of natural products. Most of these cyclisations have used carbonyl groups or their equivalents as the electrophilic centre. We were interested in the possibility of using an epoxide group as the electrophile and an allylsilane as the nucleophile in such a cyclisation, since the product would possess potentially useful functionality (*vide infra*), and it had already been demonstrated that the corresponding intermolecular reaction could be carried out.[18] The cyclisation of an epoxide-allylsilane would produce adjacent functional groups (-CH_2OH and -$CH{=}CH_2$)which are equivalent to differentiated aldehyde groups at the same time as formation of the carbocycle. Moreover the cyclisation generates a new chiral centre and it was of interest to investigate the stereoselectivity with which this was formed.

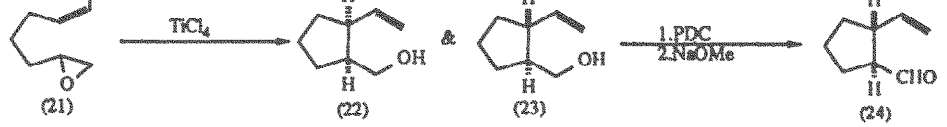
The requisite epoxide-allylsilanes were prepared as outlined in Scheme 7. One ultimate aim of this initial investigation was to utilise carbohydrates and other readily available optically active materials as sources of enantiomerically enriched cyclisation precursors and in order to accommodate this the two related routes shown in Scheme 7 were developed for the

preparation of epoxide-allylsilanes. Route *A* was investigated in order to establish the reactivity of the silyl-substituted phosphorane[19] towards lactols. In practice the route worked well for the preparation of the aldehyde (20), but the direct conversion of this aldehyde to the desired epoxide-allylsilane (21) was not particularly efficient but did give clean samples of the simple precursor (21) [no doubt a systematic study of the conversion of (20) into (21) would produce a more acceptable solution]. Route *B* was investigated as an alternative, and to determine whether the allylsilane system would survive the acidic conditions required for the removal of the acetonide group. This route was successful and proved to be the route of choice for the preparation of this simple cyclisation precursor. Both routes produced the epoxide-allylsilane (21) as a mixture of double bond isomers, approximately 4:1 Z:E as shown by high field ^{1}H nmr..

Scheme 7

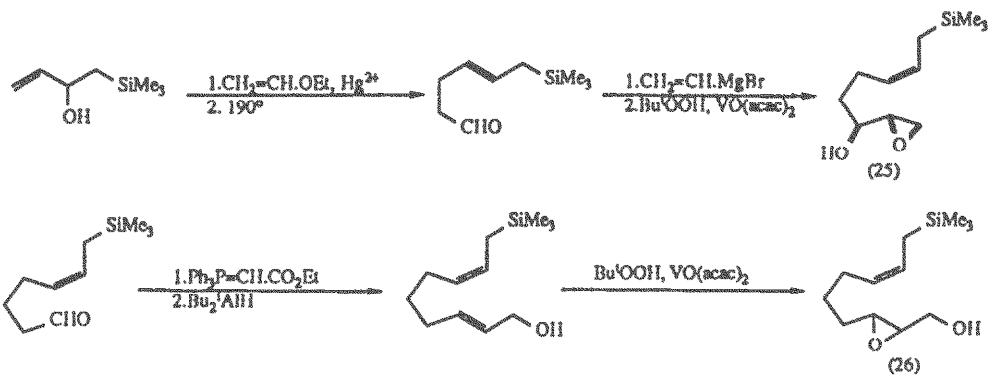


The cyclisation of epoxide-allylsilane (21) occurred on treatment with titanium tetrachloride ($TiCl_4$)[18] in dichloromethane at low temperature (~-95°) and produced a mixture of *cis*- and *trans*- isomers (22) and (23) with the *cis*- isomer predominating (~4:1). The mixture of alcohols (22) and (23) was oxidised to the corresponding mixture of aldehydes, and equilibration of this mixture produced the *trans*- isomer (24) (~10:1). This *trans*- aldehyde could be reduced to produce a highly enriched sample of the *trans*- alcohol (23).



With the success of the cyclisation of the simple precursor (21) we turned our attention to the substituted epoxide-allylsilanes (25) and (26), since these epoxides could be prepared in optically active form by the use of Sharpless epoxidation,[20] although the work presented here was carried out in the racemic series only. The preparations of the epoxide-allylsilanes (25) and (26) were straightforward, and are outlined in Scheme 8.

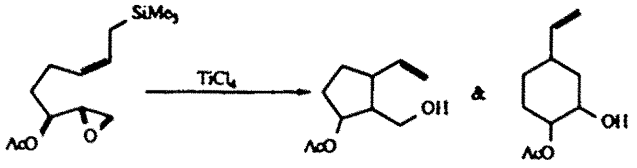
Scheme 8



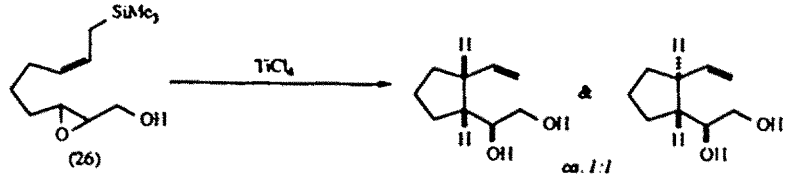
The cyclopentanes which would result from the cyclisation of (25) and (26) both bear significant relationships to natural products. The product from (25) might represent an intermediate for the synthesis of sarkomycin,[21] and the cyclopentane derived from (26) could represent the three contiguous chiral centres of brefeldin C.[22] Moreover the results of the

cyclisation of the precursors (21), (25) and (26) would form an interesting series from a mechanistic point of view.

Treatment of the epoxide-allylsilane (24) with $TiCl_4$ produced mixtures under all conditions investigated and we were unable to isolate any material which was homogeneous by high field ^1H nmr spectrometry. Similar results were obtained on cyclisation of the corresponding acetate, and in this case elemental analysis and the ^1H nmr spectrum suggested that the product was a mixture of 5- and 6-membered rings.



The cyclisation of epoxide-allylsilane (26) was much more successful, indeed the cyclisation could be carried out *without protection of the hydroxyl group and in higher yield than with the simpler precursor (21).* The product of this cyclisation was shown to be a mixture of *cis*- and *trans*- isomers by periodate cleavage of the diol to the corresponding mixture of aldehydes, both of which had been prepared previously from (21).



In conclusion this type of cyclisation can be of use for the stereoselective synthesis of functionalised cyclopentanes, and *inter alia* we are currently investigating the use of optically active epoxide-allylsilane (26) (prepared using Sharpless enantioselective epoxidation) for the synthesis of the brefeldins.

Acknowledgements. We are grateful to the S.E.R.C. for a postdoctoral research assistantship (to P.J.M.) and for research assistantships (to A.N.M. and A.T.R.), and to Dr. A.H. Davidson and Dr. I. Fleming for valuable discussions.

EXPERIMENTAL

Infra-red absorption spectra were recorded on either a Perkin-Elmer 259 or Pye-Unicam SP3-100 grating spectrophotometer. The spectra were recorded either as a thin film or as a chloroform solution in a 0.1 mm sodium chloride cell. Wavelength correction was carried out using reference absorption bands from a 0.05 mm polystyrene film. Circular dichroism spectra were recorded on a Jeol instrument. ^1H-n.m.r. were recorded using the following machines; Varian T-60 (60 MHz), Varian EM-360A (60 MHz), Perkin-Elmer R-32 (90 MHz), Bruker WM-360 (360 MHz), Bruker WH-400 (400 MHz, S.E.R.C. n.m.r. facility at Warwick), Bruker WM-360 MHz, (S.E.R.C. facility at Edinburgh), modified Bruker AC-300 (300 MHz). Samples were run as deuterochloroform solutions. Unless otherwise stated all chemical shifts were referenced to the deuterochloroform lock. For low field spectra of molecules containing a trimethylsilyl group, this resonance was taken as 0.00 δ, otherwise all spectra were referenced to tetramethylsilane (δTMS = 0.00). Electron impact mass spectra were recorded on a VG 7070H mass spectrometer. Chemical ionisation mass spectra were recorded either on a Finnigan 4500 instrument (ammonia gas), a Kratos MS-30 (methane gas) or a VG12-253 (ammonia gas) (at the S.E.R.C. facility at Swansea). X-ray structure determination was carried out at the S.E.R.C. facility at Queen Mary College, London. Data from this experiment has been deposited with the Cambridge crystallographic data centre, University Chemical Laboratory, Lensfield Road, Cambridge. Melting points were determined using an "Electrothermal" apparatus and are uncorrected. Optical rotations were measured using a Thorn automation 243 polarimeter. Concentrations are expressed in grams per 100 ml solvent. Capillary gas-chromatography was carried out on a Perkin-Elmer 8320 instrument using an SGE vitreous silica column (25QC2/BP1 0.25). Thin layer chromatography was performed with Camlab "polygram G_{254}" precoated silica-gel plates or Macherey-Nagel glass-backed plates. The plates were visualised by use of ultraviolet light, iodine or one of the following agents: methanolic phosphomolybolic acid, 10% ceric sulphate in 1N

sulphuric acid, ethanolic anisaldehyde, ethanolic vanillin or vanadium pentoxide. Silica gel 60 (particle sizes 0.040-0.063 mm) supplied by E.M. Merck was employed for flash chromatography using the procedure of Still, Khan and Mitra.[23] All solvents were distilled before use. Light petroleum refers to the fraction of b.p. 40-60°C. Ether refers to diethyl ether. Reactions were run under an atmosphere of dry nitrogen or argon. All solvents were distilled prior to use. Dry tetrahydrofuran and ether were distilled from sodium benzophenone ketyl. Dichloromethane, chloroform, diisopropylamine, benzene and ortho-xylene were dried by distillation from calcium hdyride and stored over 4Å molecular sieves. n-Butyllithium (~ 1.5M in hexanes) was supplied by Lithco Corporation and was standardised by titration, using diphenylacetic acid as indicator.[24]

(±)-E-4-Trimethylsilylbut-3-en-2-ol (10)

Magnesium (5.62 g, 0.23 mole) was covered with anhydrous ether (50 ml). Grignard reagent formation was initiated by addition of neat ethyl bromide (0.5 ml, 6.7 mmole). The reaction was maintained at a steady reflux by slow addition of ethyl bromide (17.2 ml, 0.23 mole) in anhydrous ether (140 ml). To the clear brown solution was added but-3-yn-2-ol (16) (7.99 g, 0.114 mole) as a solution in anhydrous ether (64 ml). A vigorous reaction was noted and after about half of the alcohol (16) had been added a heavy "tar-like" precipitate formed. To the two phase mixture was added trimethylsilylchloride (14.6 ml, 0.115 mole). A small scale work-up revealed some starting material left so a second equivalent of trimethylsilylchloride was added (14.6 ml, 0.115 mole) and the mixture stirred for 12 h. before quenching the reaction by tipping the whole onto iced water (300 ml). The organics were separated and the aqueous extracted with ether (3 x 100 ml). The combined organics were washed with 2 N sulphuric acid (2 x 50 ml), saturated sodium hydrogen carbonate solution (2 x 50 ml), water (1 x 50 ml), brine (1 x 50 ml), dried ($MgSO_4$), filtered and evaporated to afford (±)-4-trimethylsilyl-but-3-yn-2-ol (14) (15.39 g, 95%) as a light yellow-brown oil which was used without further purification. ν_{max} ($CHCl_3$), 3590 (O-H, free) 3400 (O-H) and 2180 cm^{-1} (C≡C), δ_H (60 MHz, $CDCl_3$), 0.00 (9H, s, Si-Me), 1.23 (3H, d, $J_{1,2}$ = 6.5 Hz, C(1)), 2.56 (1H, br.s, OH), 4.30 (1H, q, $J_{2,1}$ = 6.5 Hz, C(2)H).

To a stirred solution of sodium bis(methoxyethoxy)aluminium hydride[25] (2.07 ml, 3.4M solution in toluene, 7.04 mmole) in anhydrous ether (20 ml) at 0°C (ice bath) was added a solution of 4-trimethylsilylbut-3-yn-2-ol (506.3 mg, 3.57 mmole) in anhydrous ether (15 ml) slowly over 15 min. The reaction was stirred at 0°C for 3 h. before being quenched by the addition of a few millilitres of saturated sodium sulphate solution. The organic layer was washed with water (x 2), brine, dried ($MgSO_4$), filtered and evaporated to afford (±)-E-trimethylsilylbut-3-en-2-ol (10)[10] (404 mg, 79%) as a colourless oil sufficiently pure for immediate use. ν_{max} ($CHCl_3$), 3600 sh (O-H), 3460 br (O-H) and 1620 cm^{-1} (C=C), δ_H (90 MHz, $CDCl_3$), 0.00 (9H, s, Si-Me), 1.22 (3H, d, $J_{1,2}$ = 6.0 Hz, C(1)H), 2.93 (1H, br.s, O-H), 4.23 (1H, dq, $J_{2,1}$ = 6.0 Hz, $J_{2,3}$ = 4.0 Hz, C(2)H), 5.78 (1H, d, $J_{4,3}$ = 19.0 Hz), 6.11 (1H, dd, $J_{3,4}$ = 19.0 Hz, $J_{3,2}$ = 4.0 Hz, C(3)H). E-/Z- ratio was determined by capillary gas chromatography to be > 100:1. T.L.C.: R_f = 0.83 (ethyl acetate-light petroleum 1:1).

(R)-E 4-Trimethylsilylbut-3-en-2-ol (10)

Titanium tetraisopropoxide (2.07 ml, 6.9 mmole) and L-(+)-diethyl tartrate (1.78 ml, 10.41 mmole) were dissolved in anhydrous dichloromethane (69 ml) and cooled to -23°C (cardice/carbon tetrachloride). To this was added (±)-E-4-trimethylsilylbut-3-en-2-ol (contaminated with (±)-4-trimethylsilylbutan-2-ol) (10) (1 g, 6.94 mmole) as a solution in dichloromethane (10 ml) followed by tert-butylhydroperoxide (2.08 ml of a 2M solution in dichloromethane, 4.16 mmole). The mixture was stirred for 10 min. then transferred to the freezer at -20°C for 3 days after which it was poured into acetone (150 ml) containing water (2.1 ml) with stirring at -20°C. After 2 h. a further portion of water (2 ml) was added and stirring continued for 15 min. then the whole was filtered through a silica pad. The resulting solution was dried ($MgSO_4$), filtered and evaporated to give a crude oil. The crude was taken up in ether (50 ml) and cooled to 0°C before treating with 1 N sodium hydroxide solution (21 ml) for 1 h., with vigorous stirring. After this the organic layer was separated and washed with water, brine, dried ($MgSO_4$) and evaporated to give a crude product (987.6 mg). This was purified by flash chromatography (ethyl acetate-light petroleum 1:6) to give two fractions, fraction (A) was further purified by distillation in a Kugelrohr to afford (R)-E-trimethylsilylbut-3-en-2-ol (10) contaminated with (±)-4-trimethylsilylbutan-2-ol (279.6 mg, 28% combined yield). Spectrosocpic properties were as reported before. Fraction (B) was assigned the structure (2S,3S,4S)-3,4-epoxy-4-trimethylsilylbutan-2-ol (476.8 mg, 43%), δ_H (60 MHz, $CDCl_3$), 0.00 (9H, s, Si-Me), 1.14 (3H, d, $J_{1,2}$ = 6.0 Hz, C(1)H, 2.20 (1H, d, $J_{4,3}$ = 3.5 Hz, C(4)H), 2.5 (1H, br.s, O-H), 2.72 (1H, t, $J_{3,4}$ = 3.2 =

3.5 Hz, C(3)H), 3.80 (1H, dq, $J_{2,1}$ = 6.0 Hz, $J_{2,3}$ = 3.5 Hz, C(2)H).

The (S)-enantiomer of (10) was prepared as above but using D-(-)-diisopropyltartrate, in 29% yield (again contaminated with the saturated alcohol).

(2R)-E-4-Trimethylsilylbut-3-en-2-ol-(S)-O-acetylmandelate[26]

(2R)-E-4-Trimethylsilylbut-3-en-2-ol (25.2 mg, 0.18 mmole) together with (S)-O-acetyl-mandelic acid (52.3 mg, 0.27 mmole) and 4'-(N,N-dimethylamino)pyridine (catalytic amount) was dissolved in anhydrous dichloromethane (0.5 ml) and lowered to 0°C (ice bath). To the stirring solution was added dicyclohexylcarbodiimide (51.9 mg, 0.25 mmole) as a solution in dichloromethane (0.5 ml) dropwise over 5 min., during the addition precipitation of dicyclohexylurea was noted. The mixture was stirred at room temperature then diluted with dichloromethane and filtered through a celite pad. The organics were washed with 0.5 N hydrochloric acid (2 x 5 ml), saturated sodium hydrogen carbonate solution (2 x 5 ml), brine (1 x 5 ml), dried ($MgSO_4$), filtered and evaporated to afford (2R)-E-4-trimethylsilylbut-3-en-2-ol-(S)-O-acetyl-mandelate (58.7 mg, 105%) contaminated with a little dicyclohexylcarbodiimide. The crude product was examined by 360 MHz n.m.r. and found to be essentially one isomer. n.m.r. data as reported for the racemic case (*vide infra*).

Preparation of the mandelate esters of a mixture of E- and Z-isomers of racemic hydroxyvinylsilane (10)

In order to test the analysis of (10), a mixture of racemic *cis*- and *trans*-isomers was analysed using the following method:-

A mixture of (±)-E- and Z-4-trimethylsilylbut-3-en-2-ol (25.9 mg, 0.18 mmole) together with (S)-O-acetylmandelic acid (53.2 mg, 0.28 mmole) and 4-(N,N-dimethylamino)pyridine (catalytic amount) was dissolved in anhydrous dichloromethane (0.5 ml) and lowered to 0°C (ice bath). To the stirring solution was added dicyclohexylcarbodiimide (52.8 mg, 0.26 mmole) in dichloromethane (0.6 ml) dropwise over 5 min., during the addition precipitation of dicyclo-hexylurea was noted. The mixture was stirred at room temperature for 23 h. then diluted with dichloromethane and filtered through celite to remove the dicyclohexylurea. The organics were washed with 0.5 N hydrochloric acid (2 x 5 ml), saturated sodium hydrogen carbonate solution (2 x 5 ml), brine (1 x 5 ml), dried ($MgSO_4$), filtered and evaporated to afford a mixture of four mandelate esters (54.6 mg, 95% combined yield). The E- and Z-isomers were in a ratio of ~ 2.4:1, and the R:S ratio was 1:1, as expected.

(2R)-E-4-trimethylsilylbut-3-en-2-ol-(S)-O-acetylmandelate δ_H (360 MHz, $CDCl_3$) 0.06 (9H, s, Si-Me), 1.16 (3H, d, $J_{1,2}$ = 6.5 Hz, C(1)H), 2.19 (3H, s, O-Ac), 5.35 (1H, dqd, $J_{2,1}$ = 6.5 Hz, $J_{2,3}$ = 5.0 Hz, $J_{2,4}$ ~ 1.0 Hz, C(2)H), 5.83 (1H, dd, $J_{4,3}$ = 19.0 Hz, $J_{4,2}$ ~ 1.0 Hz, C(4)H), 5.93 (1H, s, C(5)H), 5.96 (1H, dd, $J_{3,4}$ = 19.0 Hz, $J_{3,2}$ = 5.0 Hz), 7.32-7.42 (3H, m, Ar-H), 7.44-7.52 (2H, m, Ar-H).

(2S)-E-4-trimethylsilylbut-3-en-2-ol-(S)-O-acetylmandelate δ_H (360 MHz, $CDCl_3$) -0.04 (9H, s, Si-Me), 1.31 (3H, d, $J_{1,2}$ = 6.0 Hz, C(1)H), 2.20 (3H, s, O-Ac), 5.35 (1H, m, C(2)H), 5.44 (1H, dd, $J_{4,3}$ = 19.0 Hz, $J_{4,2}$ = 1.5 Hz, C(4)H), 5.76 (1H, dd, $J_{3,4}$ = 19.0 Hz, $J_{3,2}$ = 5.0 Hz, C(3)H), 5.92 (1H, s, C(5)H), 7.34-7.42 (3H, m, Ar-H), 7.42-7.60 (2H, m, Ar-H) (2R,S)-Z-4-trimethylsilylbut-3-en-2-ol-(S)-O-acetylmandelate.

The two sets of signals for the Z-isomers cannot be distinguished and so are reported in one group. δ_H (360 MHz, $CDCl_3$) 0.08 (9H, s, Si-Me), 0.14 (9H, s, Si-Me), 1.16 (3H, d, $J_{1,2}$ = 6.5 Hz, C(1)H), 1.32 (3H, d, $J_{1,2}$ = 6.0 Hz, C(1)H), 2.20 (6H, s, both OAc), 5.57 (2H, m, both C(2)H), 5.86 (1H, s, C(5)H), 5.88 (1H, s, C(5)H), 5.99 (1H, dd, $J_{3,4}$ = 14.0 Hz, $J_{3,2}$ = 9 Hz, C(3)H), 6.19 (1H, dd, $J_{3,4}$ = 14.0 Hz, $J_{3,2}$ = 9.0 Hz, C(3)H), 7.34-7.42 (3H, m, Ar-H), 7.42-7.60 (2H, m, Ar-H).

(±)-E-N,N-Dimethyl-3-trimethylsilylhex-4-enamide (7)

(±)-E-N,N-Dimethyl-3-trimethylsilylhex-4-enamide (7) was prepared by the procedure of Jenkins, Gut, Weiler and Eschenmoser[10] in 85% yield. ν_{max} ($CHCl_3$) 1635 cm^{-1} (C=O), δ_H (360 MHz, $CDCl_3$, TMS), 0.00 (9H, s, Si-Me), 1.66 (3H, dd, $J_{6,5}$ = 5.5 Hz, $J_{6,4}$ ~ 1.0 Hz, C(6)H), 2.06 (1H, ddd, $J_{3,2B}$ = 10.5 Hz, $J_{3,4}$ = 8.0 Hz, $J_{3,2A}$ = 4 Hz, C(3)H), 2.33 (1H, dd, $J_{2A,2B}$ = 15.0 Hz, $J_{2A,3}$ = 4.0 Hz, C(2A)H), 2.43 (1H, dd, $J_{2B,2A}$ = 15.0 Hz, $J_{2B,3}$ = 10.5 Hz, C(2B)H), 2.96 (3H, s, N-Me), 3.04 (3H, s, N-Me), 5.26 (1H, dq, $J_{5,4}$ = 15.5 Hz, $J_{5,6}$ = 5.5 Hz, C(5)H), 5.34 (1H, ddq, $J_{4,5}$ = 15.5 Hz, $J_{4,3}$ = 8.0 Hz, $J_{4,6}$ ~ 1.0 Hz, C(4)H), m/z (electron impact) 213 (M^+, 15%), 212 (23), 198 (100), 184 (70), 170 (21), 159 (19), 149 (15), 145 (40), 130 (36), 129 (49), 113 (23), 112 (23), 111 (27), 102 (37). λ_{max} (EtOH) 216 nm [shoulder 232 nm]. T.L.C.: R_f = 0.22 (ethyl acetate-light petroleum 1:2).

(3S)-E-N,N-Dimethyl-3-trimethylsilylhex-4-enamide (10)

The title compound was prepared by the same procedure as used in the racemic series to give after distillation (Kugelrohr, pot temperature 97°C at 0.1 mmHg) 150.3 mg (50%).* $\Delta\varepsilon_{218} = +33.8$ dm^2 mol^{-1} (1.45 mg in 50 ml ethanol). Spectroscopic data as reported before.

*This low yield is a result of the presence of (±)-4-trimethylsilylbutan-2-ol in the starting material.

(3R)-E-N,N-Dimethyl-3-trimethylsilylhex-4-enamide (10)

The title compound (10) was prepared by the same procedure as used in the racemic series to give, after distillation (Kugelrohr, pot. temperature = 98°C at 0.1 mmHg) 128 mg (45%)* $\Delta\varepsilon_{218} = -33.14$ dm^2 mol^{-1} (1.8 mg in 50 ml ethanol). Spectroscopic data as reported before.

*This low yield is a result of the presence of (+)-4-trimethylsilylbutan-2-ol in the starting material.

(-)-(4S,5S)-5-((1S)-Hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (11)

To a solution of (3S)-E-N,N-dimethyl-3-trimethylsilylhex-4-enamide (125.6 mg, 0.59 mmole) in dichloromethane (5 ml) stirring at -20°C (cardice/carbon tetrachloride) was added m-chloroperbenzoic acid (85%) (335 mg, 1.65 mmole) as a solution in dichloromethane (10 ml) dropwise over 10 min. The solution was stirred for a further 10 min. then transferred to a freezer at -20°C for 4 days. The reaction was worked up by washing with 1 N sodium hydroxide solution (x 3), water (x 2), brine (x 1), dried ($MgSO_4$), filtered and evaporated to afford a crude oil (122 mg, 102%). This was purified by flash chromatography (ethyl acetate-light petroleum 1:3.5) to yield two fractions. Fraction (A) was shown to be (-)-(4S,5S)-5-((1S)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (11) (73.6 mg, 62%) as a colourless crystalline solid.[27] M.p. 41°C, $[\alpha]_D = -6.04$ ($CHCl_3$, 0.14), ν_{max} ($CDCl_3$), 3460 br (O-H) and 1765 cm^{-1} (C=O). δ_H (360 MHz, $CDCl_3$), δ_H (300 MHz, $CDCl_3$), 0.09 (9H, s, Si-Me), 1.26 (3H, d, $J_{7,6} = 6.0$ Hz, C(7)H), 1.65 (1H, br.s, O-H), 1.87 (1H, ddd, $J_{4,3endo} = 12.0$ Hz,* $J_{4,3exo} = 9.5$ Hz,* $J_{4,5} = 7.5$ Hz, C(4)H), 2.35 (1H, dd, $J_{3endo,3exo} = 18.0$ Hz, $J_{3endo,4} = 12.0$ Hz, C(3endoH),* 3.74 (1H, br.dq, $J_{6,5} = 7.5$ Hz, $J_{6,7} = 6.0$ Hz, C(6)H), 4.35 (1H, t, $J_{5,6} = J_{5,4} = 7.5$ Hz, C(5)H). δ_C (90.56 MHz, $CDCl_3$) - 1.7 (q, Si-CH_3), 20.6 (q, C(7)), 27.4 (d, C(4)), 30.0 (t, C(3)), 66.5 (d, C(6)), 87.3 (d, C(5)), 177.9 (s, C(2)). M/z (chemical ionisation (ammonia)) 220 [$(M^+ + NH_4)^+$, 100%], 185 (98), 130 (64), 90 (25).

*These assignments maybe reversed.

Fraction (B) was found to be a mixture of two stereoisomers (12) and (13) (16.9 mg, 14% combined yield) in a ratio of 5:1 as a crystalline solid. The major isomer was assigned the structure (4S,5R)-5((1R)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (12). ν_{max} ($CDCl_3$) (mixture) 3430 br (O-H) and 1765 cm^{-1} (C=O), δ_H (360 MHz, $CDCl_3$) 0.03 (9H, s, Si-Me), 1.14 (3H, d, $J_{7,6} = 6.5$ Hz), 1.66 (1H, ddd, $J_{4,3endo} = 11.0$ Hz,* $J_{4,3exo} = 7.0$,* $J_{4,5} = 6.0$ Hz, C(4)H), 2.28 (1H, dd, $J_{3exo,3endo} = 18.0$ Hz, $J_{3exo,4} = 7.0$ Hz, C(3exo)H),* 2.75 (1H, dd, $J_{3endo,3exo} = 18.0$ Hz, $J_{3endo,4} = 11.0$ Hz, C(3endo)H),* 2.93 (1H, br.s, O-H), 3.96 (1H, dq, $J_{6,7} = 6.5$ Hz, $J_{6,5} = 3.0$ Hz, C(6)H), 4.29 (1H, dd, $J_{5,4} = 6.0$ Hz, $J_{5,6} = 3.0$ Hz, C(5)H). δ_C (90.56 MHz, $CDCl_3$), -3.5 (m, Si-CH_3), 17.8 (q, C(7)), 21.2 (d, C(4)), 30.7 (t, C(3)), 69.0 (d, C(6)), 85.9 (d, C(5)), 178.0 (s, C(2)). M/z (chemical ionisation (methane)) (mixture 203 (M + 1, 1.7%), 185 (30), 113 (100), 73 (65). The minor stereoisomer was assigned the structure (4S,5R)-5-((1S)-hydroxyethyl)-4-trimethyl-silyldihydrofuran-2-one (13). δ_H (360 MHz, $CDCl_3$), 0.04 (9H, s, Si-Me), 1.29 (3H, d, $J_{7,6} = 6.5$ Hz), 1.84 (1H, dt, $J_{4,3endo} = J_{4,3exo} = 10.5$ Hz, $J_{4,5} = 8.0$ Hz, C(4)H), 2.32 (1H, dd, $J_{3exo,3endo} = 18.0$ Hz, $J_{3exo,4} = 10.5$ Hz, C(3_{exo})H),* 2.66 (1H, dd, $J_{3endo,3exo} = 18.0$ Hz, $J_{3endo,4} = 10.5$ Hz, C(3_{endo})H),* 2.9 (1H, br.s, O-H), 3.67 (1H, br.dq, $J_{6,7} = 6.5$ Hz, $J_{6,5} = 3.0$ Hz, C(6)H), 4.20 (1H, dd, $J_{5,4} = 8.0$ Hz, $J_{5,6} = 3.0$ Hz, C(5)H). δ_C (90.56 MHz, $CDCl_3$), -3.3 (m, Si-CH_3), 20.2 (q, C(7)), 23.3 (d, C(4)), 31.0 (t, C(3)), 68.7 (d, C(6)), 86.2 (d, C(5)), 178.0 (s, C(2)). T.L.C.: $R_f = 0.16$ (ethyl acetate-light petroleum 1:4).

*These assignments may be reversed.

(±)-(4R*,5R*)-5-((1R*)-Hydroxyethyl)-trimethylsilyldihydrofuran-2-one

The title compound was prepared as described for its antipode, to give after flash-chromatography (22) (72.3 mg, 61%) as a colourless crystalline solid. $[\alpha]_D = +4.3°$ ($CHCl_3$, C = 3.0). The stereoisomeric lactones (20) and (21) were obtained as a mixture (21.6 mg, 18%). The spectroscopic properties were as reported before.

(±)-6-Methyldihydropyr-4-en-2-one (15)

To a stirring solution of (±)-(4R*,5R*)-5-((1R*)-hydroxyethyl)-4-trimethylsilyldihydro-furan-2-one (102.2 mg, 0.51 mmole) in anhydrous chloroform (4 ml) at 40°C was added boron trifluoride etherate (0.31 ml, 2.52 mmole). The mixture was stirred at 40°C for 24 min. then quenched by the addition of saturated sodium hydrogen carbonate solution. The organic layer was separated and washed with 1:1 brine:saturated sodium hydrogen carbonate solution (2 x 2 ml), brine (1 x 2 ml), dried ($MgSO_4$), filtered and evaporated to give (±)-6-methyldihydropyr-4-en-2-one[28] (15) (56.7 mg, 100%) as light brown oil. ν_{max} ($CHCl_3$) 1730 cm^{-1} (C=O), δ_H (360 MHz, $CDCl_3$), 1.36 (3H, d, $J_{7,6}$ = 7.0 Hz, C(7)H), 2.98-3.02 (2H, m, C(3)H), 5.01 (1H, dqd, $J_{6,5}$ = 10.0 Hz, $J_{6,7}$ = 7.0 Hz, $J_{6,4}$ = 3.0 Hz, CC(6)H), 5.76 (2H, s, C(4)H and C(5)H). δ_C (90.56 MHz, $CDCl_3$), 21.5 (q, C(7)), 29.4 (t, C(3)), 75.8 (d, C(6)), 120.9 (d, C(4)), 127.5 (d, C(5)), 168.8 (s, C(2)).

This compound could also be prepared as follows:-

To a solution of (±)-(4R*,5R*)-5-((1R*)-hydroxy)-4-trimethylsilyldihydrofuran-2-one (11) (51.7 mg, 0.26 mmoles) in anhydrous tetrahydrofuran (1 ml) was added tetrabutylammonium fluoride (0.26 ml, 0.26 mmoles, 1M solution in tetrahydrofruan). The mixture was refluxed for 8 h. then diluted with ether and washed with 0.5 N hydrochloric acid (x 2), brine (x 1), dried ($MgSO_4$), filtered and evaporated to give (±)-6-methyl-dihydropyr-4-en-2-one (15) as a light brown oil (27.1 mg, 94%). N.m.r. data as reported before.

Determination of the relative stereochemistry of the ring substituents of compound (11)

To a solution of (±)-(4R*,5R*)-5-((1R*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (11) (49.1 mg, 0.24 mmole) in anhydrous tetrahydrofuran (1 ml) was added tetrabutyl-ammonium fluoride (0.25 ml, 0.25 mmole, 1M solution in tetrahydrofuran) and the mixture refluxed for 1.75 h. then the solvent evaporated to give (±)-tetrabutylammonium Z-5-hydroxyhex-3-enoic acid as a thick, light brown oil which was taken up in deuterochloroform and analysed by 360 MHz, n.m.r. This showed vinylic coupling constants consistent with a Z-double bond. δ_H (360 MHz, $CDCl_3$), 0.74 (t, J = 7.0 Hz, $N(CH_2)_3$-C<u>H</u>$_3$),* 0.96 (3H, d, $J_{6,5}$ = 6.5 Hz, C(6)H), 1.18 (sextet, J = 7 Hz, N-$(CH_2)_2$C<u>H</u>$_2$-),* 1.39 (m, NCH_2C<u>H</u>$_2$-)*, 2.57 (1H, dd, $J_{2A,2B}$ = 13.0 Hz, $J_{2A,3}$ = 7.0 Hz, C(2A)H), 3.02 (m, N-C<u>H</u>$_2$),* 4.32 (1H, quintet, $J_{5,6}$ = $J_{5,4}$ = 6.5 Hz, C(5)H), 5.30 (1H, dd, $J_{4,3}$ = 11.0 Hz, $J_{4,5}$ = 8.0 Hz, C(4)H), 5.46 (1H, br.dt, $J_{3,4}$ = $J_{3,2B}$ ~ 11 Hz, $J_{3,2A}$ = 7.0 Hz, C(3)H).

*As an excess of tetrabutylammonium fluoride was used these peaks over-integrate and so no relative integral is given.

(±)-Parasorbic acid (16)

To a solution of (±)-6-methyldihydropyr-4-en-2-one (16) (58.2 mg, 0.52 mmole) in chloroform (1 ml) was added one drop of 1,8-diazabicyclo[5.4.0]undex-7-ene and the mixture stirred at room temperature for 1 hr. At this point the solution was diluted with ether and filtered through a 1 cm silica pad, eluting with ether. The solvent was evaporated to give (±)-parasorbic acid[14] (16) (57.7 mg, 99%) as a colourless oil. ν_{max} ($CDCl_3$), 1720 cm^{-1} (C=O), δ_H (360 MHz, $CDCl_3$), 1.33 (3H, d, $J_{7,6}$ = 6.5 Hz, C(7)H), 2.19 (1H, ddt, $J_{5A,5B}$ = 19.0 Hz, $J_{5A,6}$ = 11.0 Hz, $J_{5A,3}$ = $J_{5A,4}$ = 3.0 Hz, C(5A)H), 2.29 (1H, dddd, $J_{5B,5A}$ = 19.0 Hz, $J_{5B,4}$ = 6 Hz, $J_{5B,6}$ = 4.5 Hz, $J_{5B,3}$ = 1.0, C(5B)H), 4.47 (1H, ddq, $J_{6,5A}$ = 11 Hz, $J_{6,7}$ = 6.5 Hz, $J_{6,5B}$ = 4/5 Hz, C(6)H), 5.89 (1H, ddd, $J_{3,4}$ = 10.0 Hz, $J_{3,5A}$ = 3.0 Hz, $J_{3,5B}$ = 1.0 Hz, C(3)H), 6.80 (1H, ddd, $J_{4,3}$ = 10.0 Hz, $J_{4,5B}$ = 6.0 Hz, $J_{4,5A}$ = 3.0 Hz, C(4)H). δ_C (90.56 MHz, $CDCl_3$, TMS), 20.7 (q, C(7)), 31.0 (t, C(5)), 74.4 (d, C(6)), 121.1 (d, C(3)), 145.2 (d, C(4)), 164.6 (s, C(2)).

(+)-Parasorbic acid (16)

To a solution of (-)-(4S,5R)-5-((1S)-hydroxymethyl)-4-trimethylsilyldihydrofuran-2-one (11) (52.7 mg, 0.26 mmole) in anhydrous chloroform (2 ml) was added boron trifluoride etherate (0.07 ml, 0.57 mmole) and the mixture stirred for 1.75 h. at which point a further 0.07 ml (0.57 mmole) was added. Stirring was continued for a further 50 min. then the reaction was quenched by the addition saturated sodium hydrogen carbonate solution, the organics were washed with 1:1 brine:saturated sodium hydrogen carbonate solution, dried ($MgSO_4$) and evaporated to give (+)-(6)-6-methyldihydropyr-4-en-2-one (24) as an oil. The crude oil was taken up in chloroform (1 ml) and treated with 1,8-diazabicyclo[5.4.0]-7-undecene (1 drop). After 2 h. the solvent was evaporated to leave a crude oil (52.7 mg). The crude was purified by flash chromatography (ether light-petroleum 1:1) to afford (+)-parasorbic acid (25.2 mg, 87% for the two steps). $[\alpha]_D$ = + 126.3° ($CHCl_3$, C = 2.5). Spectroscopic properties as described for the racemic compound.

(-)-(6R)-6-Methyldihydropyr-4-en-2-one (15)

The title compound was prepared as in the racemic series to afford (24) 33.7 mg (84%). $[\alpha]_D$ = -30.3° ($CHCl_3$, C = 3.2). Spectroscopic properties as described before.

(-)-Parasorbic acid (16)

The title compound was prepared as in the racemic series to afford unnatural parasorbic acid 33.4 mg (99%). $[\alpha]_D$ = - 143.6° ($CHCl_3$, C = 3.6). Spectroscopic properties as reported for the racemic compound.

(+)-(6R)-6-Methyltetrahydropyran-2-one

To a solution of (-)-parasorbic acid (16) (33.4 mg, 0.29 mmole) in ether (3 ml) was added palladium on charcoal (10%) (34.2 mg) and the mixture shaken under an atmosphere of hydrogen for 2 h. When t.l.c. showed the reaction to be complete. The solids were filtered off by passing through a pad of magnesium sulphate (anhydrous). The solvent was evaporated to give a crude oil (27.9 mg, 82%). The crude was purified by distillation (Kugelrohr) pot. temperature 80°C at 20 mmHg to give (+)-(6R)-6-methyltetrahydropyran-2-one (19.1 mg, 58%) $[\alpha]_D$ = + 31.6°C ($CHCl_3$, C = 2.0). δ_H (60 MHz, $CDCl_3$, $CHCl_3$), 1.37 (3H, d, $J_{7,6}$ = 6.5 Hz, C(7)H), 1.50-2.25 (4H, m, C(4)H and C(5)H), 2.33-2.72 (2H, m, C(3)H), 4.12-4.68 (1H, m, C(6)H).

Determination of the relative stereochemistry of the ring substituents of compounds (12) and (13)

To a solution of (±)-(4R*,5S*)-S-((1S*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (12) and its C(6) epimer (13) (5:1 mixture) (51.2 mg, 0.25 mmole) was added tetrabutyl-ammonium fluoride (0.28 ml, 0.28 mmoles, 1M in tetrahydrofuran) the mixture was refluxed for 12 h. then the solvent evaporated to give (±)-tetrabutylammonium E-5-hydroxyhex-3-enoic acid as a thick oil which was taken up in deuterochloroform and analysed by 360 MHz n.m.r. This showed a coupling constant for the vinyl protons consistent with an E-double bond δ_H (360 MHz, $CDCl_3$), 0.74 (t, J = 7 Hz, $N(CH_2)_3$-C<u>H</u>$_3$),* 0.94 (3H, d, $J_{6,5}$ = 6.5 Hz, C(6)H), 1.18 (sextet, J = 7 Hz, $N(CH_2)_3C$<u>H</u>$_3$),* 1.38 (m, $N.CH_2C$<u>H</u>$_2$-),* 2.64 (2H, d, $J_{2,3}$ = 7.0 Hz, C(2)H), 3.02 (m, N-C<u>H</u>$_2$,* 3.96 (1H, quintet, $J_{5,6} = J_{5,4}$ = 6.5 Hz, C(5)H), 5.17 (1H, dd, $J_{4,3}$ = 15 Hz, $J_{4,5}$ = 6.5 Hz, C(4)H), 5.56 (dt, $J_{3,4}$ = 15.0 Hz, $J_{3,2}$ = 7.0 Hz, C(3)H).
*As an excess of tetrabutylammonium fluoride was used these peaks overintegrate and so no relative integral is given.

(±)-*2R*,3S*)-E-N,N-2-Trimethyl-3-trimethylsilylhex-4-enamide (19)

Diisopropylamine (0.41 ml, 2.9 mmole) was dissolved in anhydrous tetrahydrofuran (6.45 ml) and cooled to 0°C. To this was added, dropwise, n-butyllithium (1.76 ml, 2.64 mmole; 1.5M in hexane). The solution was stirred at 0°C for 0.5 h. then lowered to -78°C (cardice/acetone) and a solution of (±)-E-N,N-dimethyl-3-trimethylsilylhex-4-enamide (7) (511.8 mg, 2.40 mmole) in anhydrous tetrahydrofuran (3 ml) (pre-dried over 4Å sieves) added dropwise. The mixture was stirred at -78°C for 2.5 h. then neat methyl iodide (0.49 ml, 7.92 mmole) was added. The reaction was stirred at -78°C for 3 h. then allowed to warm to room temperature overnight. The reaction was quenched by the addition of a few drops of water. The tetrahydrofuran was evaporated and the residue taken up in ether, the organics separated and washed with 1M sulphuric acid (x 2), saturated sodium hydrogen carbonate (x 1), water (1 x 5 ml), brine (1 x 5 ml), dried ($MgSO_4$), filtered and evaporated to afford a crude oil (545 mg, 100%). The crude was purified by flash chromatography (ethyl-acetate light-petroleum 1:3) to afford (±)-(2R*,3S*)-E-N,N-2-trimethyl-3-trimethylsilylhex-4-enamide (19) as a colourless oil (510.9 mg, 94%). ν_{max} (thin film) 1640 cm^{-1} (C=O), δ_H (360 MHz, $CDCl_3$), -0.07 (9H, s, Si-<u>Me</u>), 1.06 (3H, d, $J_{7,2}$ = 7.0 Hz, C(2)-<u>Me</u>, 1.65 (3H, dd, $J_{6,5}$ = 6.0 Hz, $J_{6,4}$ = 1.5 Hz, C(6)H), 1.91 (1H, dd, $J_{3,4}$ = 10.5 Hz, $J_{3,2}$ = 9.0 Hz, C(3)H), 2.79 (1H, dq, $J_{2,3}$ = 9.0 Hz, $J_{2,7}$ = 7.0 Hz, C(2)H), 2.90 (3H, s, N-<u>Me</u>), 3.04 (3H, s, N-<u>Me</u>), 5.16 (1H, ddq, $J_{4,5}$ = 15.0 Hz, $J_{4,3}$ = 10.5 Hz, $J_{4,6}$ = 1.5 Hz, C(4)H), 5.29 (1H, dq, $J_{5,4}$ = 15.0 Hz, $J_{5,6}$ = 6.0 Hz, C(5)H), m/z (chemical ionisation (methane)), 300 [$(M + SiMe_3)^+$, 20%], 256 [$(M + 29)^+$, 19] 228 [$(M + 1)^+$, 87], 212 (100.00).

(±)-(3R*,4R*,5R*)-5-((1R*)-Hydroxyethyl)-3-methyl-4-trimethylsilyldihydrofuran-2-one (20)

To a solution of (±)-(2R*,3S*)-E-N,N-2-trimethyl-3-trimethylsilylhex-4-enamide (19) (351.4 mg, 1.55 mmole) in dichloromethane (7.7 ml) stirring at -23°C (cardice/carbon tetra-chloride) was added, dropwise, a solution of m-chloroperbenzoic acid (85%) (885.1 mg, 4.36 mmole) in dichloromethane (22 ml). The solution was stirred at -23°C for a few minutes then transferred to a freezer at -20°C for 1 day. The reaction was worked up by washing with sodium

carbonate solution, water, brine, dried ($MgSO_4$), filtered and evaporated to afford a crude product (352.1 mg, 105%). The crude was purified by flash chromatography (ethyl acetate:light-petroleum 1:3) to afford two fractions. Fraction (A) was shown to be (±)-(3R*,4R*,5R*)-5-((1R*)-hydroxyethyl)-3-methyl-4-trimethylsilyldihydrofuran-2-one (20) (176 mg, 53%) as a colourless crystalline solid. A portion was crystallized from ethyl acetate and light petroleum to give an analytically pure sample (Found: C, 55.8; H, 9.5. $C_{10}H_{20}O_3Si$ requires C, 55.6; H, 9.3), m.p. 107.8-108.4°C. ν_{max} ($CHCl_3$), 1765 cm^{-1} (C=O), δ_H (400 MHz, $CDCl_3$), 0.19 (9H, s, Si-Me), 1.35 (3H, d, $J_{7,6}$ = 6.0 Hz, C(7)H), 1.37 (3H, d, $J_{8,3}$ = 8.0 Hz, C(2)-Me), 1.99 (1H, dd, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 8.0 Hz, C(4)H), 2.78 (1H, dq, $J_{3,4}$ = 9.5 Hz, $J_{3,8}$ = 8.0 Hz, C(3)H), 3.85 (1H, s, dq, $J_{6,5}$ = 9.5 Hz, $J_{6,7}$ = 6.0 Hz, C(6)H), 4.26 (1H, dd, $J_{5,6}$ = 9.5 Hz, $J_{5,4}$ = 8.0 Hz, C(5)H). M/z (chemical ionisation (methane)) 199 [(M + 1-H_2O), 16%], 155 (17), 127 (100), 73 (25). T.L.C. R_f = 0.35 (ethyl acetate light-petroleum 1:3). The structure of (20) was also determined unambiguously by X-ray crystallography.

Fraction (B) was obtained as a colourless oil (102.2 mg, 30%) and was found to be a mixture of two isomers in a ratio of approximately 1:1. One of the compounds was assigned as a γ-lactone stereoisomeric with (20), (±)-5-(1-hydroxymethyl)-3-methyl-4-trimethylsilyldihydro-furan-2-one (21). ν_{max} (thin film) (mixture of isomers) 3425 br. (O-H), 1740 cm^{-1} br (C=O). δ_H (360 MHz, $CDCl_3$), 0.12 (9H, s, Si-Me), 1.28 (3H, d, $J_{8,3}$ = 7.5 Hz, C(3)-Me), 1.32 (3H, d, $J_{7,6}$ = 6.5 Hz, C(7)H), 1.79 (1H, br.s, OH), 1.91 (1H, dd, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 7.0 Hz, C(4)H), 2.93 (1H, dq, $J_{3,4}$ = 9.5 Hz, $J_{3,8}$ = 7.5 Hz, C(3)H), 3.74 (1H, br. dq, $J_{6,7}$ = 6.5 Hz, $J_{6,5}$ = 3.5 Hz, C(6)H), 4.24 (1H, dd, $J_{5,4}$ = 7.0 Hz, $J_{5,6}$ = 3.5 Hz, C(5)H). M/z (chemical ionisation (methane)) 217 [(M + 1)$^+$, 6%], 199 (5), 155 (14), 127 (100), 73 (52). T.L.C.: R_f = 0.17 (ethyl acetate-light petroleum 1:3).

The other compound was assigned as a stereoisomer of the δ-lactone (±)-5-hydroxy-3,6-dimethyl-4-trimethylsilyltetrahydropyran-2-one (22) δ_H (360 MHz, $CDCl_3$), 0.10 (9H, s, Si-Me), 1.26 (3H, d, $J_{8,3}$ = 7.0 Hz, C(8)H), 1.35 (1H, dd, $J_{4,5}$ = 7.5 Hz, $J_{4,3}$ = 6.5 Hz, C(4)H), 1.43 (3H, d, $J_{7,6}$ = 6.0 Hz, C(7)H), 3.08 (1H, quintet, $J_{3,8}$ = $J_{3,4}$ = 7.0 Hz, C(3)H), 3.66 (1H, br.dd, $J_{5,6}$ = 9.0 Hz, $J_{5,4}$ = 7.5 Hz, C(5)H), 4.18 (1H, dq, $J_{6,5}$ = 9.0 Hz, $J_{6,7}$ = 6.0 Hz, C(6)H).

(±)-(2S*,6R*)-2,6-Dimethyldihydropyr-4-en-2-one (24)

To a solution of (±)-(3R*,4R*,5R*)-5-((1R*)-hydroxymethyl)-3-methyl-4-trimethyl-silyldihydrofuran-2-one (20) (104.4 mg, 0.48 mmole) in anhydrous chloroform (4.8 ml) was added boron trifluoride etherate (0.6 mg, 4.8 mmole). The reaction was stirred at room temperature for 12 h. then quenched by addition of saturated sodium hydrogen carbonate solution. The mixture was diluted with chloroform and washed with saturated sodium hydrogen carbonate solution (3 x 2 ml), water (1 x 2 ml), brine (1 x 2 ml), dried ($MgSO_4$), filtered and evaporated to afford (±)-(2S*,6R*)-2,6-dimethylpyr-4-en-2-one (24) (55.1 mg, 91%) as a light brown oil. Attempted purification by distillation (Kugelrohr) pot. temperature 47°C at 0.8 mbar led to substantial decomposition of (45) with only 19 mg (31%) recovered and an unidentified residue (19.4 mg). (24) showed the following properties ν_{max} (thin film) 1730 cm^{-1} (C=O), δ_H (90 MHz, $CDCl_3$, TMS) 1.38 (3H, d, $J_{7,6}$ = 7.0 Hz, C(7)H)*, 1.47 (3H, d, $J_{8,2}$ = 7.0 Hz, C(2)-Me)*, 2.84-3.20 (1H, m, C(2)H), 4.90-5.22 (1H, m, C(6)H), 5.80 (2H, s, C(4)H and C(5)H).

*These assignments may be reversed.

(±)-(2S*,6R*)-2,6-Dimethyltetrahydropyran-2-one (23). The pheromone of the carpenter-bee[16]

(±)-(2S*,6R*)-2,6-Dimethylpyr-4-en (23) (19.0 mg, 0.15 mmole) was dissolved in ether (3 ml). To this was added 10% palladium on charcoal (19.5 mg) and the mixture stirred vigorously under an atmosphere of hydrogen at room temperature for 2 h. 10 min. then the solid filtered off by passing through a pad of celite. Evaporation of the solvent gave (±) carpenter-bee pheromone (23) (17.7 mg, 92%) as a colourless oil. Attempted purification by flash-chromatography caused decomposition of the compound. The only data available is for the crude hydrogenation product. δ_H (90 MHz, $CDCl_3$, TMS), 1.22 (3H, d, J = 7.0 Hz), 1.36 (3H, d, J = 6.0 Hz), 4.34-4.59 (1H, m, C(6)H). The other protons were not clearly distinguished but the values given above are in agreement with the literature.

(±)-Ethyl E-3-trimethylsilylhex-4-enoate (8)

A mixture of E- and Z-isomers of (±)-4-trimethylsilylbut-3-en-2-ol (395.5 mg, 2.75 mmole) together with triethylorthoacetate (0.19 ml, 5.5 mmole) and propanoic acid (2 drops) were dissolved in anhydrous o-xylene and heated at 100°C for 1 h., and then raised to 136°C for 5 h. Additional triethylorthoacetate (0.3 ml, 1.8 mmole) was added and after

reflux for a further 12 h the reaction mixture was poured onto a 3 cm silica pad and then washed with light petroleum to remove the xylene. The crude product was eluted with ether:light petroleum 1:1 to give an oil 563.7 mg (96%). This oil was further purified by flash chromatography (dichloromethane-light petroleum 1:3) to afford (±)-ethyl E-3-trimethylsilylhex-4-enoate (8) (459.7 mg, 78%). ν_{max} (thin film) 1740 cm^{-1} (C=O) δ_H (60 MHz, $CDCl_3$), 0.00 (9H, s, Si-Me), 1.20 (3H, t, $J_{8,7}$ = 7.0 Hz, O-CH_2-CH_3), 1.63 (3H, br.d, $J_{6,5}$ = 4.0 Hz, C(6)H), 1.73-3.0 (3H, m, C(2)H and C(3)H), 4.10 (2H, q, $J_{7,8}$ = 7.0 Hz, O-CH_2-CH_3) 4.90-5.76 (2H, m, C(4)H and C(5)H). M/z (chemical ionisation (methane)). 231 [(M + 17], 229 [(M + 15), 12], 215 [(M + 1), 12], 214 (M^+, 17), 213 [(M - 1), 100], 185 (19), 141 (22), 73 (13).

(±)-E-3-Trimethylsilylhex-4-enoic acid (9)

To a solution of (±)-ethyl E-3-trimethylsilylhex-4-enoate (8) (195 mg, 0.19 mmoles) in ethanol:water (3 ml, 2:1 mixture) was added sodium hydroxide (40.0 mg, 1.0 mmole) and the mixture stirred at room temperature for 18 h. then most of the solvent evaporated. The residue was acidified to pH 2 and extracted with chloroform (2 x 25 ml). The organics were separated and washed with brine (x 1), dried ($MgSO_4$), filtered and evaporated to give a crude oil (176.7 mg, 104%). The crude was taken into base (1N sodium hydroxide) and after acidification to pH 2 (sulphuric acid) extracted into chloroform (2 x 25 ml). The combined organics were washed with brine (1 x 10 ml), dried ($MgSO_4$) filtered and evaporated to give (±)-E-3-trimethylsilylhex-4-enoic acid (9) (134 mg, 79%) as a colourless oil, b.p. (Kugelrohr) 83°C at 0.6 mbar (92%) recovery). ν_{max} (thin film) 3550-2300 (O-H) and 1700 cm^{-1} (C=O), δ_H (300 MHz, $CDCl_3$) -0.04 (9H, s, Si-Me), 1.62 (3H, br.d, $J_{6,5}$ = 4.5 Hz, C(6)H), 1.88-1.97 (1H, m, C(3)H), 2.30 (1H, dd, $J_{2A,2B}$ = 15.0 Hz, $J_{2A,3}$ = 11.0 Hz, C(2A)H), 2.40 (1H, dd, $J_{2B,2A}$ = 15.0 Hz, $J_{2B,3}$ = 5.0 Hz, C(2B)H), 5.20-5.35 (2H, m, C(4)H and C(5)H). M/z (chemical ionisation/ammonia)) 259 [(M + 73), 63%], 204 [$(M + NH_4)^+$, 100], 187 (27), 90 (62). T.L.C.: R_f ~ 0.5 (streaks) (ethyl acetate-light petroleum 1:3).

Reaction of (±) ethyl E-3-trimethylsilylhex-4-enoate (8) with m-CPBA

To a solution of (±)-ethyl E-3-trimethylsilylhex-4-enoate (8) (98.7 mg, 0.46 mmole) in dichloromethane (4 ml), stirring at -23°C (cardice/CCl_4) was added dropwise a solution of m-chloroperbenzoic acid (85%) (167.7 mg, 1.31 mmole) in dichloromethane (7.8 ml). The resulting mixture was stirred for 10 min. at -23°C then transferred to a freezer at -20°C for 42 h. A heavy white precipitate was formed. The reaction was worked up by dilution with dichloromethane (10 ml) then washing with 1N sodium hydroxide (3 x 5 ml), water (2 x 5 ml), brine (1 x 5 ml), dried ($MgSO_4$), filtered and evaporated to afford a crude oil (94.2 mg, 101%). The crude was analysed by capillary gas chromatography and shown to contain a 3.5:1 mixture of (13) and (12). The crude was purified by flash chormatography (ether-light petroleum 1:1) to afford a mixture of (±)-(4R*,5S*)-5-((1R*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (13) and (±)-(4R*,5S*)-5-((1S*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (12) (43.7 mg, 47%) as a colourless oil. The high field n.m.r. also revealed the presence of a small quantity of an unidentified material, otherwise spectroscopic data was as reported before.

Reaction of (±) E-3-trimethylsilylhex-4-enoic acid (9) with m-CPBA

To a solution of (±)-E-4-trimethylsilylhex-4-enoic acid (9) (69.9 mg, 0.38 mmole) in dichloromethane (3.2 ml) at -23°C (cardice/carbon tetrachloride) was added dropwise over 10 min. a solution of m-chloroperbenzoic acid (217.0 mg, 1.05 mmole) in dichloromethane (6.3 ml). The mixture was stirred for 15 mins. at -23°C, during which time a white precipitate formed, then transferred to a freezer at -20°C for 2 days. The reaction was worked up by dilution with dichloromethane and washing with 1N sodium hydroxide solution (3 x 5 ml), water (2 x 5 ml), brine (1 x 5 ml), dried ($MgSO_4$), filtered and evaporated to give a crude oil (52.3 mg, 69%). Analysis of the crude by capillary gas-chromatography revealed it to contain (12):(13):(11) in the ratio 6.5:18.1:1. This was purified by flash-chromatography (ethyl acetate-light petroleum (1:3.5) to afford two fractions. Fraction (A) was identified by capillary gas chromatography (co-injection with authentic sample) to be (±)-(4R*,5R*)-5-((1R*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (11) (2.1 mg, 3%). Fraction (B) was shown to be a mixture of (±)-(4R*,5S*)-5-((1R*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (13) and (±)-(4R*,5S*)-5-((1S*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (14) (30.3 mg, 40%). Spectroscopic properties as described before.

Determination of the stereochemistry of the ring substituents on the lactones (12) and (13) from the acid-allylsilane (9)

To a solution of a mixture of the two lactones (±)-(4R*,5S*)-5-((1R*)-hydroxyethyl)-4-trimethylsilyldihydrofuran-2-one (13) and (±)-(4R*,5S*)-5-((1S*)-hydroxyethyl)-4-trimethyl-silyldihydrofuran-2-one (12) (23.5 mg, 0.12 mmole) in anhydrous tetrahydrofuran (1 ml) was added tetrabutylammonium fluoride (0.13 ml, 0.13 mmole, 1M in tetrahydrofuran) and the mixture was refluxed for 15 h. The solvent was evaporated and the crude oil taken up in deuterochloro-form and analysed by n.m.r. and showed the same spectral characteristics as the sample of this compound previously reported. To the deuterochloroform solution was added a few drops of methyl iodide. In less than 10 min. the methyl ester was observed to have formed by n.m.r. The solution was diluted with ether and shaken vigorously with water (1 x 3 ml and 2 x 2 ml), brine (1 x 1 ml), dried ($MgSO_4$), and evaporated to afford (±)-methyl-E-5-hydroxyhex-3-enoate as an oil (8.9 mg, 52%). ν_{max} (thin film) 3370 br. (O-H) and 1735 cm^{-1} (C=O). δ_H (60 MHz, $CDCl_3$, TMS), 1.23 (3H, d, $J_{6,5}$ = 6.5 Hz, C(6)H), 2.00 (1H, br.s, O-H), 3.06 (2H, br.d, 5.0 Hz, C(2)H), 3.70 (3H, s, O-Me), 4.25 (1H, m, C(5)H), 5.35-6.05 (2H, m, C(3)H and C(4)H).

E,Z-Trimethylsilylhept-5-en-1-al (20)

n-Butyl-lithium (2.9 ml of a 1.5M solution in hexane, 1.6 mmoles) was added dropwise with stirring over 0.5 h. to a suspension of methyltriphenylphosphonium iodide (1.0 g, 2.3 mmoles) in dry THF (40 ml) at 0°C and stirred under nitrogen. The mixture was warmed to room temperature, stirred for 1 h.; re-cooled to 0°C and iodomethyltrimethylsilane (0.5 g, 2.3 mmoles) was added over 10 min., and the mixture allowed to come to room temperature. After 1 h., the reaction mixture was cooled to -78°C and treated with second equivalent of n-butyl lithium (2.9 ml of a 1.5 M solution in hexane, 1.6 mmoles). The mixture was allowed to warm to room temperature and stirred for 1.5 h. to give a dark red solution of the ylid.[19] The lactol (97) (0.24 g, 2.3 mmoles) in dry THF (10 ml) was added dropwise with stirring over 15 min. to the ylid solution at -78°C. After 0.5 h., the mixture was warmed to room temperature and stirred under nitrogen for 16 h. The mixture was washed with saturated ammonium chloride (20 ml), the aqueous layer extracted with ether (3 x 30 ml), and the combined organic extracts dried ($MgSO_4$), evaporated and distilled to give the allylsilane (0.32 g, 80%); b.p. 80°C/2 mm Hg; M/z, 186 (5.8, M^+), 73 (100.0, $Si(CH_3)_3^+$); ν_{max} 3400 (OH), 1640 (C=C); δ ($CDCl_3$) 400 MHz, 5.38 (1H, qt, Jq 10 Hz and Jt 1.6 Hz, -CH=CH-CH_2-$Si(CH_3)_3$), 5.28-5.20 (1H, m, -CH=CH-$CH_2Si(CH_3)_3$ and *trans*-isomer?), 3.62 (2H, t, J 7 Hz, -CH_2-OH), 2.00 (2H, qd, Jq = 8 Hz, Jd = 2 Hz, H-4), 1.62-1.49 (2H, m, H-7), 1.46-1.29 (4H, m, H-2 and H-3), -0.03 (9H, s, -$Si(CH_3)_3$).

Pyridinium dichromate[29] (1.94 g, 5.16 mmoles) was added to alcohol (98) (0.48 g, 2.58 mmoles) in dry dichloromethane (25 ml) and the mixture was stirred at room temperature for 18 h. The mixture was filtered through celite (using ether to wash (4 x 10 ml)), the ether was evaporated and the residue was distilled to give the aldehyde (20) (0.34 g, 71%); b.p. 80°/0.25 mm Hg; (Found: C, 64.8; H, 7.62. $C_{10}H_{20}OSi$ requires, C, 65.0; H, 7.51%); ν_{max} 1725 (C=O), 1645 (C=C); δ ($CDCl_3$) 90 MHz, 9.75 (1H, br s, -CHO), 5.60-5.00 (2H, m, -CH=CH-), 2.52 (2H, br t, J 8 Hz, H-2), 2.00 (2H, q, J 6 Hz, H-4), 1.78-1.28 (4H, m, H-3 and H-7), -0.03 (9H, s, -$Si(CH_3)_3$).

E,Z-1,2-Epoxy-8-trimethylsilyloct-6-ene (21)

Dimethylsulphoxide (20 ml) was syringed into a round bottomed flask containing sodium hydride (0.13 g, 2.8 mmoles) and trimethylsulphoxonium iodide (0.62 g, 3.0 mmoles) and stirred under nitrogen. After hydrogen gas had stopped evolving (*ca.* 20 min.),[30] the aldehyde (20) (0.40 g, 2.2 mmoles) in dimethylsulphoxide (1 ml) was added and the mixture was stirred a further 15 min. at room temperature. The mixture was warmed to 50°C for 1 h., cooled and diluted with ether (60 ml). The organic layer was washed with water (15 ml), followed by brine (10 ml), dried ($MgSO_4$), and evaporated. Flash column chromatography (ethyl acetate/petrol = 1/5) gave the epoxide (0.14 g, 33%), distillation gave an analytical sample b.p. 120°/0.2 mm Hg; (Found: C, 66.4; H, 11.07. $C_{11}H_{22}OSi$ requires C, 66.6; H, 11.10%). ν_{max} 1640 (C=C); δ ($CDCl_3$) 90 MHz, 5.58-5.05 (2H, m, -CH=CH-), 2.90 (1H, br m, H-2), 2.68 (1H, t, $J_{1A,2}$ = $J_{1A,1B}$ = 5 Hz, H-1A), 2.42 (1H, dd, $J_{1B,2}$ 2.5 Hz, $J_{1A,1B}$ 5 Hz, H-1B), 2.15-1.80 (2H, m, H-5), 1.70-1.28 (6H, m, H-3, H-4, H-8), -0.03 (9H, s, Si $(CH_3)_3$).

Acetonide of 5,6-dihydroxyhexanal

Toluene-4-sulphonic acid (0.96 g, 5.1 mmoles) was added to a solution of 1,2,6-hexane-triol (100) (8.0 g, 59.6 mmoles) in freshly distilled acetone (100 ml) and the mixture stirred at room temperature for 20 h. Solid sodium hydrogen carbonate was added and the mixture was stirred for 0.5 h., filtered and evaporated to give the crude acetonide (9.53 g, 92%); ν_{max} 3440 (OH), 1150 (C-O); δ ($CDCl_3$) 90 MHz, 4.30-3.90 (2H, m, H-5 and H_A-6), 3.75-3.35 (3H, m, H-1 and H_B-6), 2.75 (1H, br s, disappears upon addition of D_2O, -OH), 1.80-1.45 (6H, m, H-2, H-3 and H-4), 1.40 (3H, s, -CH_3), 1.35 (3H, s, -CH_3).

Pyridinium dichromate (4.3 g, 11.5 mmoles) was added to a solution of alcohol (1.0 g, 5.8 mmoles) in freshly distilled dichloromethane (60 ml) and the mixture stirred at room temperature for 16 h. Ether (40 ml) was added and the mixture was stirred for *ca.* 0.5 h. THe mixture was filtered through celite, filtered through $MgSO_4$, evaporated and flash column chromatography (ethyl acetate/petrol = 1/5) gave the aldehyde (0.87 g, 88%); (Found: C, 62.3; H, 9.11. $C_9H_{16}O_3$ requires C, 62.7; H, 9.30%); ν_{max} 1720 (C=O), 1150 (C-O); δ ($CDCl_3$) 90 MHz, 9.75 (1H, br s, -CHO), 4.25-3.90 (2H, m, H-5 and H_A-6), 3.75-3.30 (1H, m, H_B-6), 2.70-2.30 (2H, m, H-2), 1.90-1.45 (4H, m, H-3 and H-4), 1.40 (3H, s, -CH_3), 1.35 (3H, s, -CH_3).

Acetonide of E,Z-8-trimethylsilyloct-6-ene-1,2-diol

n-Butyl lithium (5.2 ml of a 1.5 M solution in hexane, 8.8 mmoles) was added dropwise to a suspension of methyltriphenylphosphonium iodide (3.54 g, 8.8 mmoles) in dry THF (28 ml) at 0°C and stirred under nitrogen. The mixture was warmed to room temperature, stirred for 1 h., re-cooled to 0°C and iodomethyltrimethylsilane (1.87 g, 8.8 mmoles) was added and the mixture allowed to come to room temperature. After 1 h., the reaction mixture was cooled to -78°C and treated with a second equivalent of n-butyl lithium (5.2 ml of a 1.5 M solution in hecane; 8.8 mmoles). The mixture was allowed to warm to room temperature and stirred for 1.5 h. to give a dark red solution of the ylid.[19] The aldehyde (102) (1.37 g, 0.80 mmoles) in dry THF (2 ml) was added dropwise with stirring over 10 mins. to the ylid solution at -78°C. After 0.5 h., the mixture was warmed to room temperature and stirred under nitrogen for 16 h. The mixture was then washed with saturated ammonium chloride (50 ml), extracted with ether (3 x 50 ml) and the ether extract washed with brine (50 ml), dried ($MgSO_4$), evaporated and distilled to give the allylsilane (1.27 g, 63.5%); b.p. 80°C/2 mmHg; (Found: C, 63.4; H, 10.82. $C_{14}H_{28}O_2Si$ requires C, 63.6; H, 10.93%). ν_{max} 1650 (C=C); δ ($CDCl_3$) 90 MHz, 5.60-5.00 (2H, m, -CH=CH-), 4.20-3.90 (2H, m, H_A-1 and H-2), 3.70-3.35 (1H, m, H_B-1), 2.20-1.80 (2H, m, H-5), 1.70-1.15 (6H, m, H-3, H-4 and H-8), 1.38 (3H, s, -CH_3), 1.32 (3H, s, -CH_3), -0.03 (9H, s, -$Si(CH_3)_3$).

E,Z-8-Trimethylsilyloct-6-ene-1,2-diol

A solution of the actonide (0.61 g, 2.4 mmoles) in concentrated hydrochloric acid (0.2 ml)/water (0.2 ml)/methanol (1.0 ml)/chloroform (2.0 ml) was stirred at room temperature for 18 h. The mixture was neutralised with solid sodium hydrogen carbonate and the solvent evaporated. The residue was extracted with ether (3 x 30 ml), dried ($MgSO_4$), evaporated, and flash column chromatography (ethyl acetate/petrol = 1/9) gave the diol (0.38 g, 73%); (Found: C, 61.4; H, 9.63. $C_{11}H_{21}O_2Si$ requires C, 61.1; H, 9.72%); M/z, 216 (0.5, M^+), (100.0, $SiMe_3^+$); ν_{max} 3300 (OH), 1640 (C=C); δ ($CDCl_3$) 90 MHz, 5.55-5.05 (2H, m, -CH=CH-), 3.85-3.25 (3H, m, H-1 and H-2), 2.30-1.82 (4H, very br m, H-5 and 2X-OH), 1.65-1.25 (6H, H-3, H-4 and H-8), -0.03 (9H, s, -$Si(CH_3)_3$).

E,Z-8-trimethylsilyl-oct-6-ene-1,6-1,2-diol-1-p-toluenesulphonate

p-Toluenesulphonyl chloride (0.74 g, 3.9 mmoles) was added to a solution of the diol (0.76 g, 3.5 mmoles) in dry dichloromethane (4 ml), followed by freshly distilled pyridine (0.56 g, 7.0 mmoles) and the mixture was stirred at 0°C for *ca.* 2 h. The mixture was allowed to warm to room temperature and stirred a further 18 h. The solvent was evaporated and pyridine (1.0 ml)/water (0.5 ml) was added and the mixture was stirred a further 1 h. (to destory any excess p-toluene sulphonyl chloride). The mixture was extracted with ether (3 x 20 ml) and the ether extract washed with 2N hydrochloric acid (10 ml), aqueous sodium hydrogen carbonate (10 ml), brine (15 ml), dried ($MgSO_4$), evaporated, and flash column chromatography (ethyl acetate/petrol = 1/1) gave the tosylate. (1.06g, 83.4%); (Found: C, 58.7; H, 8.12. $C_{18}H_{30}O_4SiS$ requires C, 58.4; H, 8.10%); ν_{max} 3400 (OH), 1640 (C=C), δ ($CDCl_3$) 90 MHz, 7.80 (2H, d, J 8 Hz, -OTs), 7.35 (2H, d, J 8 Hz, -OTs), 5.55-5.00 (2H, m, -CH=CH-), 4.20-3.60 (3H, m, H-1 and H-2), 2.40 (3H, s, -CH_3), 2.20 (1H, br s, -OH), 2.05-1.20 (8H, m, H-3, H-4, H-5 and H-8), -0.03 (9H, s, -$Si(CH_3)_3$).

E,Z-1,2-Epoxy-8-trimethylsilyloct-6-ene (21)

To a solution of tosylate (0.48 g, 1.3 mmoles) in dry chloroform (4.9 ml), a solution of sodium (0.13 g, 5.7 mmoles) in methanol (2.4 ml) was added dropwise at 0°C, the mixture was allowed to warm to room temperature and stirred for 20 h. The mixture was extracted with ether (2 x 20 ml) and the ether extract washed with saturated ammonium chloride (15 ml), brine (15 ml), dried ($MgSO_4$), evapoarted and flash column chromatography (ethyl acetate/petrol = 1/5) gave the epoxide (21) (0.20 g, 77.5%), identical to that prepared previously.

cis,trans-1-Hydroxymethyl-2-vinylcyclopentane (22)/(23)

A cold solution (~ -33°C) of titanium (IV) chloride (0.48 ml of a 1.8M solution in methylene chloride, 0.9 mmoles) was added to a solution of epoxide (21) (0.16 g, 0.79 mmoles) in dry methylene chloride[18] (4 ml) at -90°C and the mixture stirred under nitrogen for 1 h. Saturated sodium hydrogen caronate (10 ml) was added at -90°C and the mixture was brought to room temperature and filtered through celite (*ca.* 2 cm) [using methylene chloride (3 x 15 ml) to wash]. The organic layer was washed with brine (15 ml), dried ($MgSO_4$), evaporated and flash column chromatography (ethyl acetate/petrol 1/1) gave the cyclopentanes (22) and (23) (0.06 g, 55.4%); (Found: C, 76.0; H, 10.99. $C_8H_{14}O$ requires C; 76.2; H, 11.11%); M/z 126 (11, M^+), 108 (97, M-H_2O), 98 (27, M-C_2H_4), 95 (67, M-CH_2OH), 94 (16), 93 (94), 83 (19), 82 (37), 81 (21), 80 (61), 79 (100%). ν_{max} 3380 (OH), 1640 (C=C); δ ($CDCl_3$) 360 MHz, 5.81 (1H, m, -C<u>H</u>=CH_2), 5.02 (1H, br d, J_{trans} = 16.5 Hz, HC=C<u>H</u>$_A$H$_B$); 4.96 (1H,br d, J_{cis} = 10.8 Hz, HC=CH$_A$<u>H</u>$_B$), 3.55 (1H, dd, J_{AB} = 8.3 and $J_{A,1}$ = 18 Hz, -C<u>H</u>$_A$H$_B$-OH), 3.42 (1H, dd, J_{AB} = 8.3 and $J_{A,1}$ = 18 Hz, -C<u>H</u>$_A$H$_B$-OH), 3.42 (1H, dd, J_{AB} = 8.3 Hz and $J_{B,1}$ = 18 Hz, -CH$_A$<u>H</u>$_B$-OH), 2.63 (1H, m, H-2), 2.13 (1H, m, H-1), 2.02 (1H, very br s, OH), 1.85-1.25 (6H, m, H-3, H-4 and H-5).

1-Trimethylsilylbut-3-en-2-ol

Chloromethyltrimethylsilane (1.23 g, 10 mmoles) was added to a suspension of magnesium turnings (0.29 g, 12 mmoles) in dry ether (5 ml) and the mixture was stirred at room temperature under nitrogen. (A few crystals of iodine were used to initiate the reaction). When the magnesium had dissolved, crotonaldehyde (0.70 g, 10 mmoles) in dry ether (5 ml) was added dropwise to the Grignard reagent at 0°C, the mixture was allowed to warm to room temperature and stirred a further 6 h. The mixture was diluted with ether (25 ml) and the organic layer was washed with brine (10 ml), dried ($MgSO_4$) and evaporated to give the alcohol (1.40 g, 77.8%); ν_{max} 3450 (OH), 1660 (C=C); δ ($CDCl_3$) 90 MHz, 5.85 (1H, ddd, $J_{A,2}$ = 7.5 Hz, J_{AB} = 10 Hz and J_{AC} = 17.5 Hz, <u>H</u>$_A$C=CH$_B$H$_C$), 5.10 (1H, d, J_{AC} = 17.5 Hz, H$_A$C=CH$_B$<u>H</u>$_C$), 4.95 (1H, d, J_{AB} = 10 Hz, H$_A$C=C<u>H</u>$_B$H$_C$), 4.22 (1H, q, J 7.5 Hz, -C<u>H</u>(OH)-), 1.65 (1H, br s, disappears upon addition of D_2O, -OH).

E-6-Trimethylsilylhex-4-en-1-al

Mercuric acetate (0.16 g, 0.5 mmoles) was added to a solution of the silane (0.39 g, 2.5 mmoles) in freshly distilled ethyl vinyl ether (4 ml) and the mixture was stirred at room temperature under nitrogen for 18 h. The mixture was washed with brine (5 ml) and the aqueous solution extracted with ether (2 x 15 ml). The organic extracts were dried ($MgSO_4$), evaporated and distilled to give the vinyl ether (0.29 g, 63.0%); b.p. 54-58°C/2 mm Hg; ν_{max} 1660 (C=C); δ ($CDCl_3$) 90 MHz, 6.25 (1H, dd, J_{cis} = 7 Hz and J_{trans} = 15 Hz, H_2C=C<u>H</u>-O-), 5.75 (1H, ddd, J_{AB} = 8 Hz, J_{cis} = 10 Hz and J_{trans} = 18 Hz, H_2C=CH_A-C<u>H</u>$_B$(CH_2)-), 5.18 (1H, br d, J_{cis} = 10 Hz, H$_D$<u>H</u>$_C$ = CH_A-C<u>H</u>$_B$(CH_2)-), 5.10 (1H, br d, J_{trans} = 18 Hz, H$_D$<u>H</u>$_C$=CH_A-C<u>H</u>$_B$(CH_2)-), 4.38-3.72 (3H, m, H_2C=CH-O- and H_2C=C<u>H</u>$_A$-C<u>H</u>$_B$(CH_2)-), 1.15-0.65 (2H, m, -C<u>H</u>$_2$-Si(CH_3)$_3$), -0.03 (9H, s, -Si(CH_3)$_3$).

The neat silane (0.20 g, 1.2 mmoles) was heated for 1 h. at 190°C. Distillation gave the aldehyde (0.15 g, 52.6%); b.p. 90°C/2 mm Hg; M/z, 170 (0.5, M^+), 116 (28.0), 101 (65.2), 74 (11.0), 73 (100.0, $SiMe_3^+$); ν_{max} 1720 (C=O), 1660 (C=C); δ ($CDCl_3$) 90 MHz, 9.75 (1H, br s, -CHO), 5.50-5.00 (2H, m, -CH=CH-), 2.60-2.05 (4H, m, H-2 and H-3), 1.50-1.25 (2H, m, -C<u>H</u>$_2$-Si(CH_3)$_3$); 0.00 (9H, s, -Si(CH_3)$_3$).

8-Trimethylsilyl-6E-octa-1,6-diene-3-ol

Vinylmagnesium bromide (11 ml of a 1.0 M solution in THF, 11.0 mmoles) was added dropwise to a solution of the aldehyde (0.94 g, 5.5 mmoles) in dry THF (10 ml) and -78°C and stirred under nitrogen for 0.5 h. The mixture was warmed to room temperature and stirred a further 16 h. Saturated sodium hydrogen carbonate (10 ml) was added to the

mixture followed by extraction with ether (2 x 20 ml). The ether extract was washed with water (10 ml), brine (10 ml), dried ($MgSO_4$), evaporated and flash column chromatography (ethyl acetate/petrol = 1/3) gave the alcohol (0.68 g, 61.9%); (Found: C, 67.1; H, 11.22. $C_{11}H_{22}OSi$ requires C, 66.6; H, 11.11%); ν_{max} 3350 (OH), 1650 (C=C); δ ($CDCl_3$) 90 MHz, 6.18-5.05 (5H, m, vinyl H), 4.15 (1H, q, J 6 Hz, -CH(OH)-), 2.15-1.40 (6H, m, H-4, H-5 and H-8), 0.00 (9H, s, $-Si(CH_3)_3$).

6E-1,2-Epoxy-8-trimethylsilyl-oct-6-en-3-ol (25)

A solution of t-butyl hydroperoxide in benzene was prepared as follows. Benzene (7.2 ml) was added to t-butyl hydroperoxide (2.8 ml in 70% water, 20 mmoles) and the lower layer was discarded. The mixture was then dried over magnesium sulphate. Vanadyl bis-acetylacetonate (7 mg) was added to a solution of the alcohol (0.60 g, 3.1 mmoles) in dry benzene (15 ml), followed by t-butyl hydroperoxide solution (2.3 ml, 4.6 mmoles) and the mixture was stirred at room temperature under nitrogen for 18 h. The mixture was washed with brine (5 ml) and the aqueous solution extracted with ethyl acetate (3 x 15 ml). The combined organic extracts were dried ($MgSO_4$), evaporated, and flash column chromatography (ethyl acetate/petrol = 1/3) gave the epoxide (25) (0.21 g, 33%); (Found: C, 62.0; H, 10.08. $C_{11}H_{22}O_2Si$ requires C, 61.7; H, 10.28%); M/z, 214 (2.1), 117 (25.9), 75 (89.2), 74 (19.4), 73 (100.0, $SiMe_3^+$); ν_{max} 3430 (OH), 1250; δ ($CDCl_3$) 90 MHz, 5.65-5.00 (2H, m, -CH=CH-), 4.12-3.75 (1H, m, H-3), 3.08-2.60 (3H, m, H-1 and H-2), 2.30-1.30 (6H, m, H-4, H-5 and H-8), 0.00 (9H, s,-$Si(CH_3)_3$).

Attempted ring closure of the epoxy-allylsilane (25)

A cold solution (~ -33°C) of titanium (IV) chloride (0.31 ml of a 1.8M solution in methylene chloride, 0.56 mmoles) was added to a solution of the epoxysilane (25) (0.11 g, 0.51 mmoles) in freshly distilled methylene chloride (2.8 ml) at -78°C and stirred under nitrogen for 1 h. The mixture was poured into saturated sodium hydrogen carbonate (3 ml), filtered through celite (using methylene chloride (3 x 10 ml) to wash). The organic extract was washed with brine (10 ml), dried ($MgSO_4$) and evaporated, flash column chromatography (ethyl acetate/petrol = 5/1) failed to give any fractions homogeneous by ^1H n.m.r. The major fraction (0.03 g, 41%) shows hydroxyl stretching (3460 cm^{-1}) and C=C stretching (1640 cm^{-1}). The 360 MHz ^1H n.m.r. shows the presence of vinyl protons at δ 5.80 and δ 4.95, a singlet at δ 3.93 (1H), a doublet at δ 3.65 (1H), a broad singlet at δ 2.88 (-CH_2-OH) and multiplets at δ 2.00 (2H), δ 1.73 (1H) and δ 1.50 (6H).

Acetate of 6E-1,2-Epoxy-8-trimethylsilyloct-6-ene-3-acetate (25)

Freshly distilled triethylamine (54.5 mg, 0.54 mmoles) was added dropwise to a solution of alcohol (25) (96 mg, 0.45 mmoles) in dry methylene chloride (1.4 ml), followed by acetic anhydride (50.3 mg, 0.49 mmoles) and 4-dimethylaminopyridine (6 mg, 0.04 mmoles) and the mixture stirred at room temperature for 1 h. The mixture was poured into saturated ammonium chloride (10 ml) and extracted with methylene chloride (3 x 15 ml). The organic extract was washed with dilute hydrochloric acid (10 ml), saturated sodium hydrogen carbonate (2 x 10 ml), brine (10 ml), dried ($MgSO_4$), evaporated, and flash chromatography (ethyl acetate/petrol = 1/3) gave the acetate (95 mg, 83.0%); (Found: C, 61.0; H, 9.30. $C_{13}H_{24}O_3Si$ requires C, 60.9; H, 9.37%); ν_{max} 1740 (C=O), 1240; δ ($CDCl_3$) 90 MHz, 5.60-5.05 (2H, m, -CH=CH-), 4.75 (1H, q, J 6 Hz, H-3), 3.10-2.82 (1H, m, H-2), 2.80-2.60 (2H, m, H-1), 2.10 (3H, s, $COCH_3$), 2.05-1.18 (6H, m, H-4, H-5 and H-8), 0.00 (9H, s, -$Si(CH_3)_3$).

Attempted ring closure of acetate

A cold solution (~ -33°C) of titanium (IV) chloride (0.5 ml of a 0.8M solution in methylene chloride, 0.42 mmoles) was added to a solution of epoxysilane (99 mg, 0.39 mmoles) in dry methylene chloride (2.5 ml) at -78°C and stirred under nitrogen for 1 h. The mixture was warmed to room temperature and stirred a for a further 1 h. The mixture was then poured into saturated sodium hydrogen carbonate (5 ml), filtered through celite (using methylene chloride (3 x 20 ml) to wash). The organic extract was washed with brine (10 ml), dried ($MgSO_4$) and evaporated and flash column chromatography (ethyl acetate/petrol = 1/1) gave a mixture of products, none homogeneous by ^1H n.m.r. The major fraction (31 mg, 43.5%) provided the following physical data. Found: C, 65.0; H, 8.41; $C_{10}H_{16}O_3$ equires C, 65.2; H, 8.69%). ν_{max} 3450 (OH), 1720 (C=O), 164- (C=C). The 360 MHz ^1H n.m.r. shows the presence of vinyl protons at δ 5.70 and δ 5.00, a multiplet at δ 3.75 (-CH-OAc), two acetate groups at δ 2.60 and δ 2.50, and multiplets at δ 2.40 (6H).

Methyl 2E,7E/Z-9-Trimethylsilylnona-2,7-dienoate

Dried methyl triphenylphosphoranylideneacetate (0.57 g, 1.63 mmoles) was added to a solution of aldehyde (20) (0.30 g, 1.63 mmoles) in freshly distilled benzene (10 ml) and the mixture was stirred at room temperature for 16 h. The benzene was evaporated and ether (10 ml) was added to the residue. The mixture was filtered through a layer of magnesium sulphate (~ 2 cm), evaporated and flash column chromatography (ethyl acetate/petrol = 1/3) gave the ester (0.30 g, 77.0%); (Found: C, 65.0; H, 9.89. $C_{13}H_{24}O_2Si$ requires C, 65.0; H, 10.00%); ν_{max} 1710 (C=O), 1650 (C=C); δ ($CDCl_3$) 90 MHz, 7.18 (1H, dt, J 8 and 16 Hz, H_3COOC-CH=C<u>H</u>-), 5.85 (1H, br d, J 16 Hz, H_3COOC-<u>H</u>C=CH-), 5.65-5.10 (2H, m, -C<u>H</u>=C<u>H</u>-$CH_2Si(CH_3)_3$), 3.75 (3H, s, OCH_3), 2.38-1.90 (4H, m, H-4 and H-6), 1.65-1.30 (4H, m, H-5 and H-9), -0.03 (9H, s, -$Si(CH_3)_3$).

2E,7E/Z-9-Trimethylsilylnona-2,7-dien-1-ol

Diisobutyl aluminium hydride (2.8 ml of a 1M solution in hexane, 4.2 mmoles) was added to a solution of the ester (0.34 g, 1.4 mmoles) in freshly distilled hexane (2.4 ml) and the mixture was stirred under nitrogen at room temperature for 16 h. The mixture was diluted with ether (30 ml) and saturated ammonium chloride (15 ml) added, the mixture was then filtered. The organic layer was washed with brine (10 ml), dried ($MgSO_4$), evaporated, and flash column chromato-graphy (ethyl acetate/petrol = 1/3) gave the alcohol (0.27 g, 89.5%); (Found: C, 67.6; H, 11.25. $C_{12}H_{24}OSi$ requires C, 67.9; H, 11.30%); ν_{max} 3400 (OH), 1610 (C=C), 1150 (C-O); δ ($CDCl_3$) 90 MHz, 5.78-5.58 (2H, m, HO-CH_2-C<u>H</u>=C<u>H</u>-), 5.52-5.10 (2H, m, -C<u>H</u>=C<u>H</u>-CH_2-$Si(CH_3)_3$), 4.12 (2H, d, J 4 Hz, H-1), 2.25-1.94 (4H, m, H-4 and H-6), 1.80-1.30 (4H, m, H-5 and H-9), 0.00 (9H, s, -$Si(CH_3)_3$).

2E,7E/Z-*trans*-2,3-Epoxy-9-trimethylsilylnon-7-en-1-ol (26)

A solution of t-butyl hydroperoxide in benzene was prepared as follows. Benzene (7.2 ml) was added to t-butyl hydroperoxide (2.8 ml 70% in water, 20 mmoles) and the lower layer was discarded. The organic layer was then dried ($MgSO_4$). Vanadyl bis-acetylacetonate (6 mg) was added to a solution of alcohol (0.29 g, 1.38 mmoles) in dry benzene (7.3 ml), followed by the t-butyl hydroperoxide solution (1.0 ml, 2.07 mmoles) and the mixture was stirred at room temperature under nitrogen for 18 h. The mixture was diluted with ethyl acetate (40 ml) and washed with water (10 ml), brine (10 ml), dried ($MgSO_4$), evaporated, and flash column chromatography (ethyl acetate/petrol = 1/3) gave the epoxide (26) (0.19 g, 60.3%); (Found: C, 63.5; H, 10.45. $C_{12}H_{24}SiO_2$ requires C, 63.2; H, 10.53%); ν_{max} 3410 (OH), 1640 (C=C), 1250; δ ($CDCl_3$) 90 MHz, 5.54-4.95 (2H, m, -HC=CH-), 3.75 (1H, br d, J 12 Hz, -$CH_{\underline{A}}H_{\underline{B}}$-OH), 3.45 (1H, br d, J 12 Hz, -$CH_{\underline{A}}H_{\underline{B}}$-OH), 2.98-2.72 (2H, m, H-2 and H-3), 2.48 (1H, br s, -OH), 1.90 (2H, q, J 6 Hz, H-6), 1.60-1.15 (6H, m, H-4, H-5 and H-9), -0.05 (9H, s, -$Si(CH_3)_3$).

1-(1,2-Dihydroxyethyl)-2-vinylcyclopentanes (27) or (28)

A cold solution (~ -33°C) of titanium (IV) chloride (0.5 ml of a 0.93M solution in dichloromethane, 0.47 mmoles) was added to a solution of epoxide (26) (97 mg, 0.42 mmoles) in dry methylene chloride (2.5 ml) at -78°C and stirred under nitrogen at this temperature for 1.5 h. The mixture was poured into saturated sodium hydrogen carbonate (5 ml) and filtered through celite (using methylene chloride (2 x 20 ml) to wash). The organic layer was washed with brine (10 ml), dried ($MgSO_4$), evaporated and flash column chromatography (ethyl acetate/petrol = 5/1) gave the cyclopentanes (27) and (28) (40 mg, 60.3%), as a mixture of *cis*- and trans-isomers (*ca.* 2:3) (Found: C, 68.9; H, 10.15. $C_9H_{16}O_2$ requires C, 69.2; H, 10.26%); ν_{max} 3350 (OH), 1640 (C=C); δ ($CDCl_3$) 90 MHz, 5.70 (1H, m, -C<u>H</u>=CH_2), 5.15-4.80 (2H, m, -CH=C<u>H</u>$_2$), 3.75-3.35 (3H, m, C<u>H</u>$_2$(OH)-C<u>H</u>(OH)-), 3.02 (2H, br s, 2X-OH), 2.70-2.12 (1H, m, H-2), 2.05-1.15 (7H, m, H-1, H-3, H-4 and H-5).

cis/trans-2-Vinylcyclopentane-1-carboxaldehyde

Sodium periodate (104 mg, 0.49 mmoles) was added to a solution of the diols (27) and (28) (38 mg, 0.24 mmoles) in carbon tetrachloride (0.1 ml)/acetonitrile (0.1 ml)/water (0.15 ml) and the mixture stirred at room temperature for 4 h. The mixture was filtered and extracted with methylene chloride (3 x 15 ml). The organic extract was washed with saturated sodium hydrogen caronate (5 ml), brine (10 ml), dried ($MgSO_4$) and evaporated to give the *cis*- and *trans*-aldehydes (25 mg, 83%, *cis:trans* = 2:3); ν_{max} 1720 (C=O), 1640 (C=C); δ ($CDCl_3$) 360 MHz, *cis-isomer*:- 9.67 (1H, d, J 2.5 Hz, -CHO), 5.85 (1H, ddd, $J_{A,C}$ = 17.5 Hz, $J_{A,B}$ = 10 Hz, $J_{A,2}$ = 8 Hz, $\underline{H}_A$C=C$H_{\underline{B}}H_{\underline{C}}$), 5.12 (1H, br d, $J_{A,C}$ =

17.5 Hz, $H_AC{=}CH_B\underline{H_C}$), 5.05 (1H, br d, $J_{A,B}$ = 10 Hz, $H_AC{=}C\underline{H_B}H_C$, 2.96 (1H, br quintet, $J_{2,A} = J_{2,1} = J_{2,3}$ = 8 Hz, H-2), 2.88 (1H, m, H-1), 2.10-1.44 (6H, m, H-3, H-4 and H-5); *trans-isomer*:- 9.2 (1H, d, J 2.5 Hz, -CHO), 5.80 (1H, ddd, $J_{A,C}$ = 17.5 Hz, $J_{A,B}$ = 10 Hz, $J_{A,2}$ = 7.5 Hz, $\underline{H_A}C{=}CH_BH_C$), 5.06 (1H, br d, $J_{A,C}$ = 17 Hz, $H_AC{=}CH_B\underline{H_C}$), 5.00 (1H, br d, $J_{A,B}$ = 10 Hz, $H_AC{=}C\underline{H_B}H_C$), 2.74 (1H, br quintet, $J_{2,A} = J_{2,1} = J_{2,3}$ = 7.5 Hz, H-2), 2.54 (1H, qd, $J_{1,1'}$ = 2.5 Hz, $J_{1,2} = J_{1,5}$ = 7.5 Hz, H-1), 2.10-1.44 (6H, m, H-3, H-4 and H-5). These two aldehydes could also be prepared from the alcohols (22) and (23) by oxidation with PDC in dichloromethane.

trans-2-Vinylcyclopentane-1-carboxaldehyde (24)

A solution of sodium (10 mg, 0.4 mmoles) in methanol (4 ml) was added dropwise to the *cis*- and *trans*-aldehydes (50 mg, 0.4 mmoles) and the mixture was stirred at room temperature for 2 h. The mixture was diluted with ether (40 ml) and washed with saturated ammonium chloride (10 ml), brine (10 ml), dried ($MgSO_4$) and evaporated carefully to give the *trans*-aldehyde (24) (40 mg, 90% crude yield. The ^1H n.m.r. spectrum was identical to that reported in the previous experiment.

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