Diastereofacial Selectivity in Diels–Alder Reactions of a Diene having a Stereogenic Centre carrying a Silyl Group Adjacent to the Diene System

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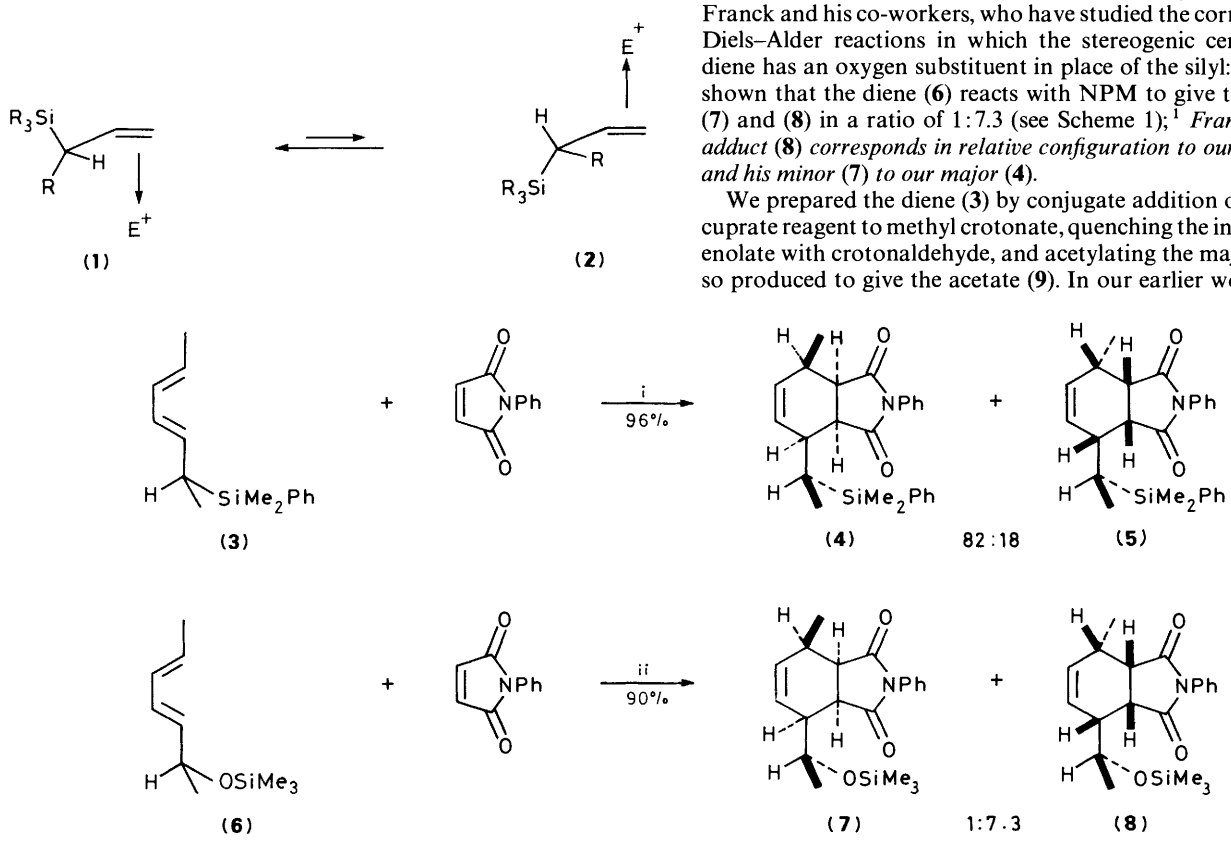
The dienylmethylsilane (**3**) reacts with *N*-phenylmaleimide to give the adducts (**4**) and (**5**) in a ratio of 82:18, the major product having come from reaction with diastereoface selectivity in the sense (**18**). The same diene, however, reacts with dimethyl acetylenedicarboxylate in the opposite sense (**19**) to give only the adduct (**25**). These results are not only complementary to each other but are also complementary to the reactions of the dienes (**6**) and (**22**), having an oxygen substituent on the stereogenic centre in place of the silyl group, where the major reaction of (**6**) with *N*-phenylmaleimide is known to take place in the sense (**20**), and the major reaction of (**22**) with dimethyl acetylenedicarboxylate in the opposite sense (**21**).

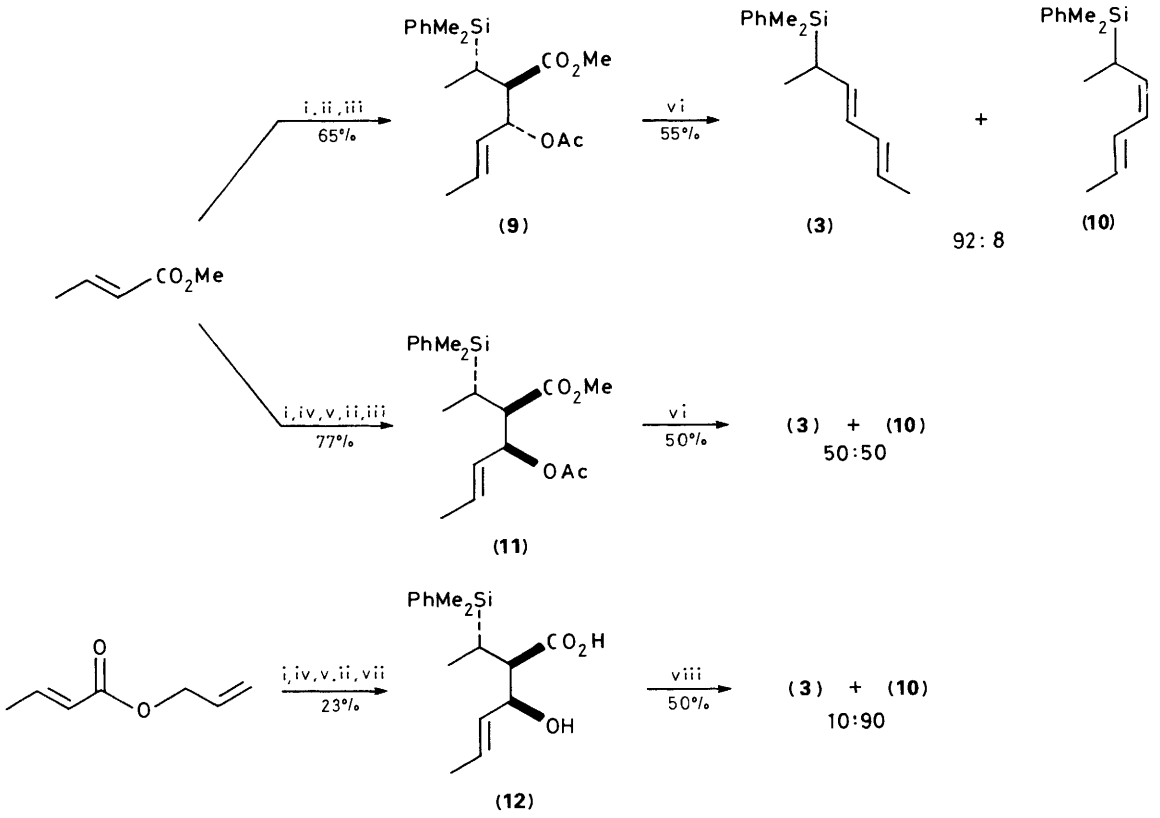
Among the many aspects of the Diels–Alder reaction to excite attention recently has been the effect of a stereogeneic centre adjacent either to the diene system[1,2–5] or to the dienophile double bond.[6] When the three substituents on the stereogenic centre are well-differentiated sterically and/or electronically, there is some hope that one such centre can induce up to *four* new stereogenic centres in one step—a remarkably attractive proposition.

In a growing body of work,[7,8] we have shown that a stereogenic centre carrying a silyl group, a carbon group, and a hydrogen atom is often very effective in controlling the diastereoface selectivity of reactions at an adjacent double bond in the general sense (**1**). This conformation, or something close to it, with the hydrogen 'inside,' is probably the most highly populated, and the two groups on the stereogenic centre, the silyl and the carbon group R, are still well-differentiated, both sterically and electronically. The alternative conformation (**2**), or something close to it, with the R group 'inside' is usually less well populated (but see below), and it leads only to minor products. We had some hope therefore that Diels–Alder reactions would be stereochemically well-controlled by such a stereogenic centre. We now report that this is indeed the case, the diene (**3**) reacting with *N*-phenylmaleimide (NPM) to give the adducts (**4**) and (**5**) in a ratio of 82:18 (see Scheme 1).[9] In carrying out this work, we had the added incentive that we would be able to compare our results directly with those of Franck and his co-workers, who have studied the corresponding Diels–Alder reactions in which the stereogenic centre in the diene has an oxygen substituent in place of the silyl: they, have shown that the diene (**6**) reacts with NPM to give the adducts (**7**) and (**8**) in a ratio of 1:7.3 (see Scheme 1);[1] *Franck's major adduct* (**8**) *corresponds in relative configuration to our minor* (**5**), *and his minor* (**7**) *to our major* (**4**).

We prepared the diene (**3**) by conjugate addition of our silylcuprate reagent to methyl crotonate, quenching the intermediate enolate with crotonaldehyde, and acetylating the major alcohol so produced to give the acetate (**9**). In our earlier work on this



Scheme 1. *Reagents:* i, C_6H_6, 60°, 2 d; ii, C_6H_6, r.t., 10 d



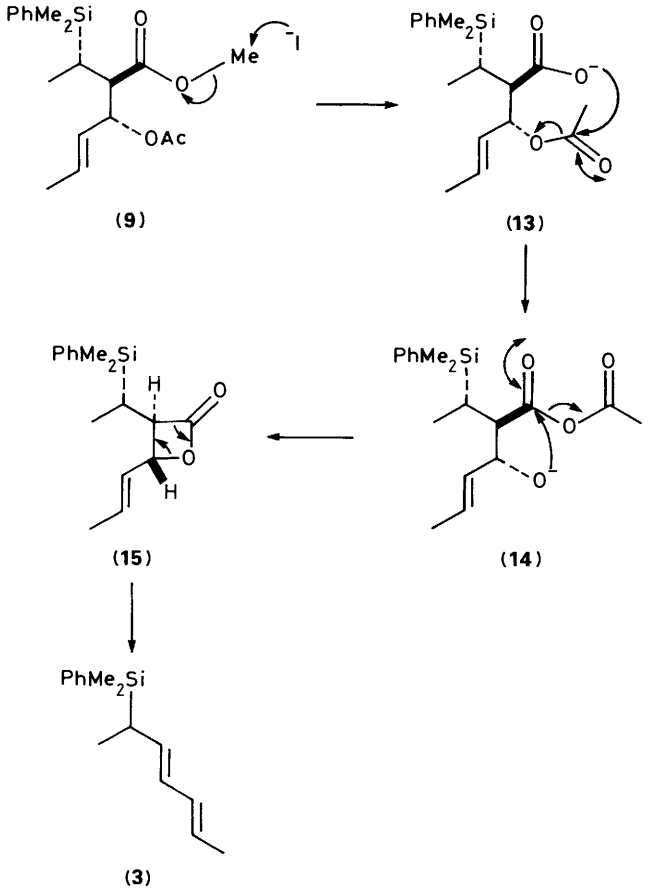
Scheme 2. *Reagents:* i, $(PhMe_2Si)_2CuLi{\cdot}LiCN$; ii, MeCH=CHCHO; iii, Ac_2O, Et_3N, DMAP; iv, NH_4Cl, H_2O; v, LDA, THF; vi, LiI, Py; vii, Me_2CuLi; viii, $PhSO_2Cl$, Py

method of synthesizing allylsilanes,[10] heating esters like (**9**) with lithium iodide in pyridine[11] merely removed the methyl group from the ester. In this series, however, where we have a double bond present in (**9**), we find that cleavage of the methyl ester group using iodide ion also sets off the decarboxylative elimination to give the diene (**3**) directly, together with a small amount of its 3-*Z*,5-*E* isomer (**10**) (see Scheme 2). This method of allylsilane synthesis is not as highly stereospecific as our earlier method,[10] since (**11**), the diastereoisomer of (**9**), gave the two dienes in equal amounts. In order to confirm our assignments of structure to these two dienes, we also synthesized a mixture rich in the *Z*,*E*-isomer (**10**), using the longer but more highly stereospecific route from allyl crotonate by way of the β-hydroxy acid (**12**). The new reaction, insofar as it is stereospecific, is, *syn* stereospecific, presumably taking place by S_N2 removal of the methyl group, intramolecular anhydride formation (**13**)→(**14**), β-lactone formation (**14**)→(**15**), and *syn* cycloreversion (**15**)→(**3**) (see Scheme 3). Whatever, the mechanism, it is usefully quick to carry out when it is stereoselective, as in the reaction (**9**)→(**3**). Furthermore, only the *E*,*E*-isomer (**3**) takes part in the Diels–Alder reaction, and contamination of the starting material by the *Z*,*E*-isomer (**10**) is no problem.

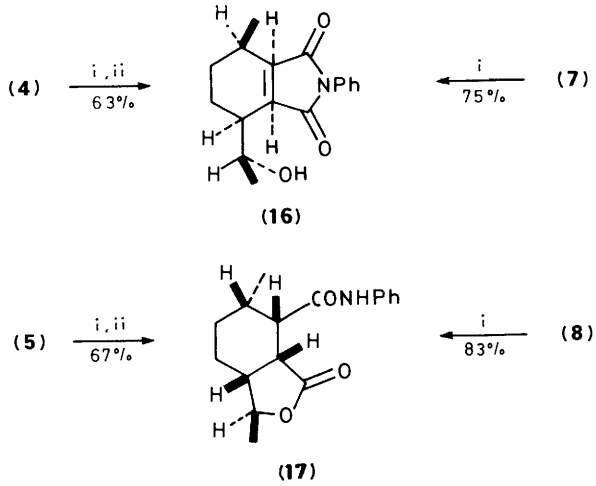
We proved the stereochemistry of the adducts by separately hydrogenating the double bond of each diastereoisomer (**4**) and (**5**), and then converting the phenyldimethylsilyl group in each into a hydroxy group using mercuric acetate in peracetic acid.[12] The products were the imide (**16**) and the lactone (**17**) (see Scheme 4). This difference in the products, readily seen in the i.r. spectrum, already alerted us to the stereochemistry of our adducts, because lactone formation is known to be easy only when the methyl group on the lactone ring is *exo* in the bicyclic system, as in (**17**).[1,2] To be certain of this assignment, we also repeated Franck's reaction (**6**)→(**7**) + (**8**), and hydrogenated the adducts in methanol to give the same compounds (**16**) and (**17**). The major adduct from our reaction unmistakably correlated with the minor from Franck's, and *vice versa*.

The sense of the diastereoselectivity in our reaction is that expected by analogy with some of our earlier work, summarised in the picture (**1**): the major product comes from reaction in the sense (**18**), in which the hydrogen atom on the stereogenic centre is 'inside' and the dienophile has approached *anti* to the silyl group. The Si–C bond is electronically activating to the diene system, raising the energy of the HOMO; it will therefore be conjugated with the diene system at the time of reaction. In contrast, the O–C bond will be deactivating, and will lie substantially out of conjugation, as in conformation (**20**) or something close to it. The result is a complete change of diastereoface selection when the substituent is changed from the electropositive, and hence σ-donating, silyl group to the electronegative, and hence σ-withdrawing, oxygen group.

In the diene (**3**), the carbon group on the stereogenic centre, a methyl group, is as small as it can be, and only a hydrogen atom is placed *cis* to the stereogenic centre. When these particular features are present, the alternative conformation (**19**) is also well-populated, and attack on the upper surface of (**19**) is even less hindered than attack on the lower surface of (**18**). Allylsilanes having this pair of features are, in general, stereochemically unpredictable in their reactions. Known reactions of such allylsilanes include: (i) hydroboration with 9-BBN, which is, as far as we can detect, entirely selective in the sense (**1**),[7] (ii) epoxidation and Simmons-Smith reaction, which are selective in favour of reaction in the sense (**1**) to the extent of *ca.* 2:1,[13,14] (iii) hydroboration with borane, which is almost perfectly unselective,[7] and (iv) reaction with osmium tetraoxide[13] and cycloaddition to nitrile oxides,[15] both of which are selective for reaction in the sense (**2**) to the extent of about 2:1. All these reactions are, in one sense or another,

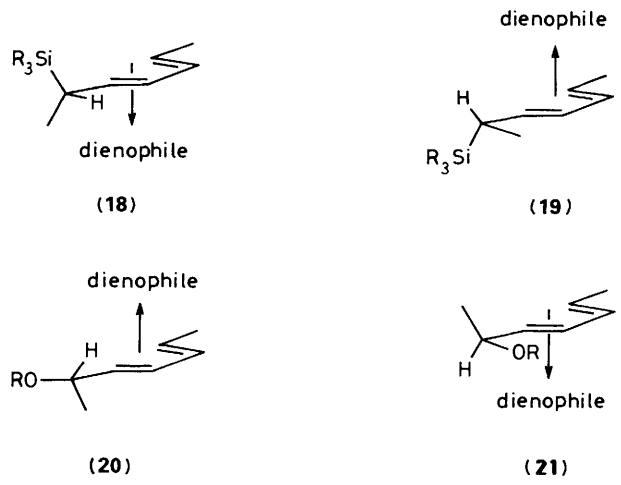


Scheme 3.



Scheme 4. *Reagents:* i, H_2, Pd/C, MeOH; ii, $Hg((OAc)_2$, AcO_2H, AcOH

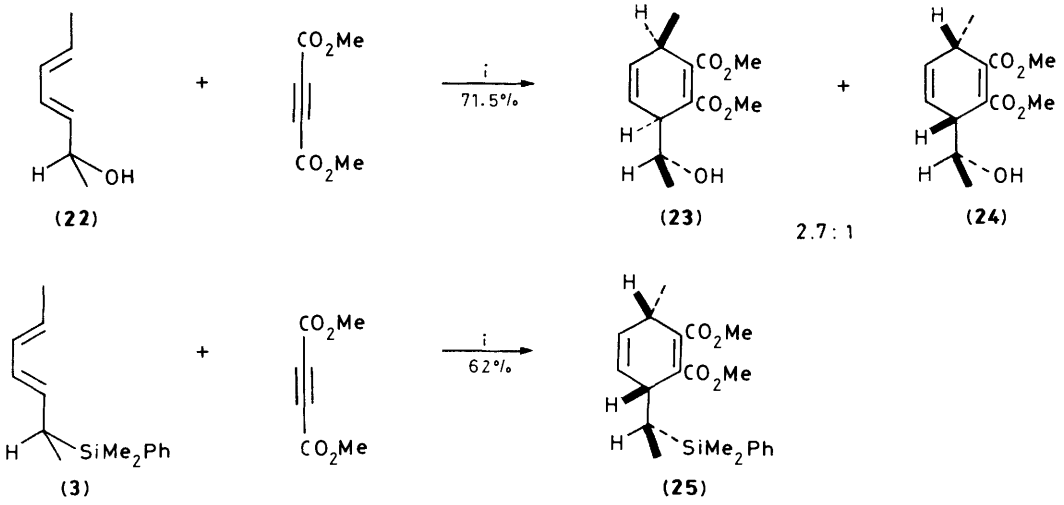
cycloadditions, but there is no discernible pattern to them that would have allowed us to predict the diastereoselectivity of the Diels–Alder reaction. When the carbon group on the stereogenic centre is larger than a methyl group, or when the substituent *cis* to the stereogenic centre is larger than hydrogen, the general pattern summarised as (**1**) becomes much more reliable,[13,14] presumably because this conformation is then overwhelmingly the most highly populated.



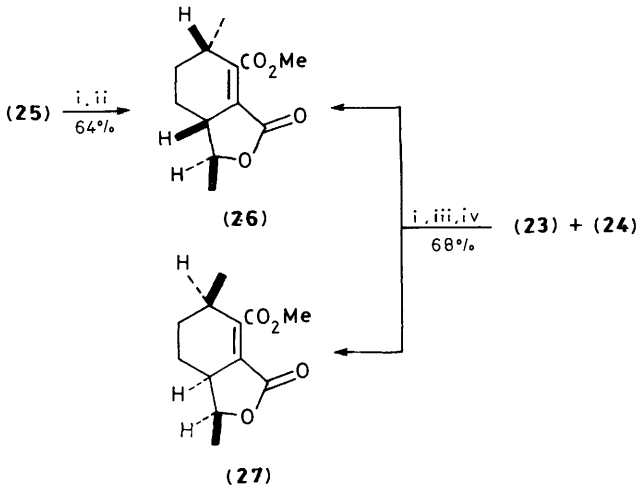
The same problem arises with Franck's diene (**6**), where the conformation (**20**), with the oxygen substituent 'outside,' is not obviously better than the alternative conformation (**21**), in which the oxygen is 'inside.' Indeed, he finds reaction in the sense (**21**) when he uses dimethyl acetylenedicarboxylate (DMAD) as the dienophile and the free alcohol (**22**) as the diene (see Scheme 5). [The earlier diene (**6**) is the silyl ether of this diene.] The adducts (**23**) and (**24**) were formed in a ratio of 2.7:1,[1] and Kozikowski and his co-workers, also using acetylenic dienophiles, have made similar observations.[3] Naturally, we also looked at the Diels–Alder reaction of DMAD with our diene (**3**), and again found[16] that it gives diastereoselectivity complementary to that of Franck's, and hence opposite in sense to that which we had observed with NPM. We were only able to detect one adduct (**25**), which corresponds to reaction taking place only in the sense (**19**). The configuration follows from correlation of our only adduct with Franck's minor adduct, using the same sequence of reactions as before, except that the adducts (**23**) and (**24**) were inseparable, and we, like Franck,[1] were only able to separate the mixture after hydrogenation and lactonisation had given the lactones (**26**) and (**27**) (see Scheme 6). The lactone (**26**) was the same as that derived from his minor adduct (**24**), and clearly different from the lactone (**27**) derived from his major adduct (**23**), and the yields of the two lactones (18 and 50%, respectively) were high enough to make the assignments unambiguous. To be absolutely certain, we also carried out an *X*-ray crystal structure determination on the lactone (**26**), derived from the adduct (**25**). With only one adduct detectable, the reaction (**3**)→(**25**) joins the end of the list given above as the *most* selective reaction known of an allylsilane taking place in the sense (**2**)≡(**19**). In this case, it is easy to explain why this particular dienophile should be so different: the ester group of DMAD will experience a much stronger repulsion from the methyl group on the stereogenic centre in conformation (**18**) than the carbonyl group of NPM does, since the latter, in the *endo* transition state, is under the diene system and hence further away from the stereogenic centre. In a reaction taking place in the sense (**19**), the corresponding interaction is with a hydrogen atom, and therefore as small as it can be. This argument is similar to one used to explain the pattern of results in the oxygen series,[3] but the full story there is much more complicated,[17] and probably not yet fully resolved.[4,18]

Experimental

(4E)-(2SR,3SR)-*Methyl* 2-[(1RS)-1-*Dimethyl(phenyl)silylethyl*]-3-*hydroxyhex*-4-*enoate*.—Methyl crotonate (2.9 g, 29



Scheme 5. *Reagent:* i, toluene, reflux, 2 d



Scheme 6. *Reagents:* i, H_2, Pd/C, MeOH; ii, $Hg(OAc)_2$, AcO_2H, AcOH; iii, TsOH, MeOH; iv, t.l.c.

mmol), in dry tetrahydrofuran (THF) (20 ml) was added dropwise to a stirred solution of bisdimethyl(phenyl)silyl cuprate[8] [32 mmol, based on copper(I) cyanide] under nitrogen at −78 °C and stirring continued for 2 h. A solution of freshly distilled crotonaldehyde (3.4 g, 48 mmol) in dry THF (5 ml) was added and stirred for a further 1 h at −78 °C. The reaction mixture was quenched with basic aqueous ammonium chloride (20 ml) and extracted with ether (3 × 50 ml). The combined extracts were washed with basic aqueous ammonium chloride (2 × 10 ml) and brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Flash chromatography (SiO_2; hexane–EtOAc, 5:1, v/v) gave the (2SR,3SR,1′RS)-β-*hydroxy ester* (6.0 g, 68%), corresponding in relative configuration to the acetate (**9**): R_F (hexane–EtOAc, 5:1, v/v), 0.21, $\nu_{max.}$(film) 3 460 (OH), 1 715 (CO), 1 242 (SiMe), and 1 103 cm^{-1} (SiPh); δ($CDCl_3$) 7.53—7.31 (5 H, m, Ph), 5.61 (1 H, m, MeC*H*=CH), 5.34 (1 H, ddq, *J* 15, 6 and 1.6 Hz, MeCH=C*H*), 4.26 (1 H, m, C*H*OH), 3.36 (3 H, s, CO_2Me), 2.38 (1 H, dd, *J* 4.2 and 9.5 Hz, $CHCO_2$), 1.65 (3 H, d, *J* 5 Hz, *Me*CH=CH), 1.07 (3 H, d, *J* 7.5 Hz, *Me*CHSi), and 0.30 and 0.25 (3 H each, s, $SiMe_2$) (Found: *M* − C_4H_7O, 235.1157. $C_{13}H_{19}O_2Si$ requires *M*, 235.1154); *m*/*z* 235 (8.6%, *M* − C_4H_7O) and 135 (100, $SiMe_2Ph$). The minor product (1.5 g, 16%) was the (2*SR*,3*RS*,1′*RS*)-isomer, corresponding in relative configuration to the acetate (**11**), identical with the sample prepared as described below. The relative configuration of these products was assigned by analogy with our earlier work.[10]

Methyl 3-*Dimethyl(phenyl)silylbutyrate.*—Methyl crotonate (3 g, 30 mmol) was added to the silyl-cuprate reagent (33 mmol), as described above, the mixture quenched with aqueous ammonium chloride (15 ml), and extracted with ether (3 × 25 ml). The combined ether extracts were washed with brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Chromatography (SiO_2; hexane–EtOAc, 10/1, v/v) gave the *ester* (6.7 g, 96%) b.p. 100—102 °C/0.5 mmHg, identical with a sample prepared earlier by Kilburn:[19] R_F (light petroleum–EtOAc, 5:1, v/v) 0.42; $\nu_{max.}$($CDCl_3$) 1 730 (CO) and 1 580 cm^{-1} (Ph); δ($CDCl_3$) 7.55—7.31 (5 H, m, Ph), 3.62 (3 H, s, OMe), 2.39 (1 H, dd, *J* 15 and 4 Hz, $CH_AH_BCO_2Me$), 2.07 (1 H, dd, *J* 15 and 11 Hz, $CH_AH_BCO_2Me$), 1.43 (1 H, m, MeC*H*), 0.98 (3 H, d, *J* 7 Hz, MeC), and 0.29 (6 H, s, $SiMe_2$) (Found: M^+, 236.1228. $C_{13}H_{20}O_2Si$ requires *M*, 236.1233); *m*/*z* 236 (5%, M^+), 221 (20, *M* − Me), and 135 (100, $PhMe_2Si$).

(4E)-(2SR,3RS)-*Methyl* 2-[(1RS)-1-*Dimethyl(phenyl)silylethyl*]-3-*hydroxyhex*-4-*enoate.*—Methyl 3-dimethyl(phenyl)-silylbutyrate (2.12 g, 9 mmol), in dry THF (15 ml) was added dropwise to a stirred solution of LDA (8 mmol) in THF (15 ml), under nitrogen at −78 °C, over 15 min and the solution stirred for 20 min. A solution of crotonaldehyde (1.4 g, 20 mmol) in dry THF (5 ml) was added dropwise and the mixture was stirred for a further 1 h at −78 °C. The reaction mixture was quenched with aqueous ammonium chloride (15 ml) and extracted with ether (3 × 25 ml). The combined ether extracts were washed with brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Flash column chromatography (SiO_2; hexane–EtOAc, 5:1, v/v) gave the same β-hydroxy esters as above in a ratio of 92:8 (^1H n.m.r.) (2.37 g, 86%), now in favour of the *alcohol* corresponding in relative configuration to the acetate (**11**): R_F (hexane–EtOAc, 5:1, v/v) 0.2; $\nu_{max.}$(film) 3 470 (OH), 1 720 (CO), 1 245 (SiMe), and 1 105 cm^{-1} (SiPh); δ($CDCl_3$) 7.54—7.30 (5 H, m, Ph), 5.69—5.53 (2 H, m, CH=CH), 4.24 (1 H, m, C*H*OH), 3.48 (3 H, s, CO_2Me), 2.65 (1 H, dd, *J* 7 and 7.6 Hz, $CHCO_2$), 1.66 (3 H, d, *J* 5 Hz, *Me*CH=CH), 1.57 (1 H, br s, OH), 1.45 (1 H, quintet, *J* 7.6 Hz, CHSi), 0.98 (3 H, d, *J* 7.6 Hz, *Me*CHSi), and 0.29 and 0.28 (3 H each, s, $SiMe_2$) (Found: *M* − C_4H_7O, 235.1173. $C_{13}H_{19}O_2Si$ requires *M*, 235.1154); *m*/*z* 235 (21%, *M* − C_4H_7O), 135 (59, $SiMe_2Ph$), and 69 (100, C_4H_5O).

(4E)-(2SR,3SR)-*Methyl* 3-*Acetoxy*-2-[(1'RS)-1'-*dimethyl*-(*phenyl*)*silylethyl*]-*hex*-4-*enoate* (**9**).—The β-hydroxy ester (5.1 g, 16.6 mmol), triethylamine (3 ml, 20 mmol), and 4-dimethylaminopyridine (DMAP) (0.4 g, 3.2 mmol) were dissolved in dry ether (100 ml). Acetic anhydride (2 ml, 20 mmol) was added and the mixture stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure and the residue dissolved in ether (100 ml). The solution was then washed with 1M hydrochloric acid (25 ml), saturated aqueous sodium hydrogencarbonate (25 ml), and brine (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Chromatography (SiO_2, hexane–EtOAc, 10:1, v/v) of the residue gave the *acetate* (5.5 g, 96%) as a viscous oil, R_F (hexane–EtOAc, 10:1, v/v) 0.22; $\nu_{max.}$(film) 1 730 (CO), 1 235 (OCOMe), and 1 105 cm^{-1} (SiPh); δ($CDCl_3$) 7.51—7.31 (5 H, m, Ph), 5.72 (1 H, dq, *J* 15.2 and 6.7 Hz, MeC*H*=CH), 5.44 (1 H, t, *J* 8 Hz, CHOAc), 5.28 (1 H, ddq, *J* 15.2, 8, and 1.6 Hz, MeCH=C*H*), 3.50 (3 H, s, CO_2Me), 2.56 (1 H, dd, *J* 7.9 and 6.1 Hz, $CHCO_2$), 1.97 (3 H, s, OCOMe), 1.68 (3 H, dd, 1.6 and 6.6 Hz, *Me*CH=CH), 1.38 (1 H, quintet, *J* 7.6 Hz, CHSi), 1.01 (3 H, d, *J* 7.6 Hz, *Me*CHSi), and 0.33 and 0.27 (3 H each, s, $SiMe_2$) (Found: *M* − Me − CO_2, 289.1636. $C_{17}H_{25}O_2Si$ requires *M*, 289.1624); *m*/*z* 289 (2.6%, *M* − Me − CO_2), 273 (19, *M* − Me − $MeCO_2H$), 235 (92, $MeCHSiMe_2PhCHCO_2Me$), 135 (100, $SiMe_2Ph$), and 69 (82, C_4H_5O).

(4E)-(2RS,3SR)-*Methyl* 3-*Acetoxy*-2-[(1SR)-1-*dimethyl*-(*phenyl*)*silylethyl*]*hex*-4-*enoate* (**11**).—This compound was prepared similarly to give the diastereoisomeric *acetate* (93%), R_F (hexane–EtOAc, 10:1, v/v) 0.32, $\nu_{max.}$(film) 1 732 (CO), 1 230 (OCOMe), and 1 110 cm^{-1} (SiPh); δ($CDCl_3$) 7.49—7.30 (5 H, m, Ph), 5.83—5.86 (2 H, m, CH=CH), 5.54 (1 H, dd, *J* 6.4 and 8.1 Hz, CHOAc), 3.41 (3 H, s, CO_2Me), 2.73 (1 H, dd, *J* 6.4 and 10.2 Hz, $CHCO_2$), 1.98 (3 H, s, OCOMe), 1.70 (3 H, d, *J* 5.5 Hz, *Me*CH=CH), 1.33 (1 H, dq, *J* 10.2 and 7.5 Hz, CHSi), 0.95 (3 H, d, *J* 7.4 Hz, *Me*CHSi), and 0.27 and 0.25 (3 H, each, s, $SiMe_2Ph$) (Found: *M* − Me, 333.1529. $C_{18}H_{25}O_4Si$ requires *M*, 333.1522); *m*/*z* 333 (1.2%, *M* − Me), 235 (50, $MeCHSiMe_2PhCHCO_2Me$), 135 (100, $SiMe_2Ph$), and 69 (56, C_4H_5O).

(3E,5E)-(*Hept*-3,5-*dien*-2-*yl*)*dimethyl*(*phenyl*)*silane* (**3**).—The acetate (**9**) (2.2 g, 6.32 mmol) and anhydrous lithium iodide (30 mmol) were refluxed in anhydrous pyridine (30 ml) under nitrogen for 24 h. The pyridine was evaporated off under reduced pressure, and the residue dissolved in ether (20 ml), washed with water (10 ml), dried ($MgSO_4$), and evaporated under reduced pressure. Flash chromatography (SiO_2, hexane) gave an inseparable mixture of the *dienes* (**3**) and (**10**) (0.8 g, 55%) in a ratio of 92:8 (^{1}H-n.m.r.); R_F (hexane) 0.6; $\nu_{max.}$(film) 1 250 (SiMe), 1 110 (SiPh), and 980 cm^{-1} (CH=CH); δ($CDCl_3$) 7.51—7.32 (5 H, m, Ph), 6.05 (1 H, ddq, *J* 10, 15 and 1.3 Hz, MeCH=C*H*), 5.86 (1 H, dd, *J* 10 and 15 Hz, MeCH=CHC*H*), 5.57 (1 H, dd, *J* 7.2 and 15 Hz, MeCHSiC*H*), 5.5 (1 H, dq, *J* 15 and 6.5 Hz, MeC*H*=CH), 1.84 (1 H, quintet, *J* 7 Hz, CHSi), 1.73 (3 H, d, *J* 6.6 Hz, *Me*CH=CH), 1.05 (3 H, d, *J* 7.2 Hz, *Me*CHSi), and 0.26 (6 H, s, $SiMe_2$) (Found: M^+, 230.1509. $C_{15}H_{22}Si$ requires *M*, 230.1490).

Decarboxylative Elimination with the Ester (**11**).—The acetate (**11**) (2 g, 5.74 mmol) treated in the same way gave the same dienes (**3**) and (**10**) (0.66 g, 50%) in a ratio of 1:1 (^{1}H-n.m.r.), with peaks clearly present from both isomers.

Allyl 3-*Dimethyl*(*phenyl*)*silylbutyrate*.—Allyl crotonate (1.26 g, 10 mmol) in THF (5 ml) was added to the dimethyl(phenyl)-silyl-cuprate reagent (12 mmol) and the mixture quenched with aqueous ammonium chloride, as described above. A similar work-up gave the β-*silyl ester* (1.6 g, 61%) as an oil, R_F (hexane–EtOAc, 10:1, v/v) 0.36; $\nu_{max.}$(film) 1 745 (CO), 1 255 (SiMe), and 1 115 (SiPh); δ($CDCl_3$) 7.51—7.34 (5 H, m, Ph), 5.97—5.84 (1 H, m, C*H*=CH_2), 5.33—5.19 (2 H, m, CH=CH_2), 4.52 (2 H, dt, *J* 5.8 and 1.3 Hz, OCH_2), 2.41 (1 H, dd, *J* 4 and 15.3 Hz, $CH_ACH_BCO_2$), 2.08 (1 H, dd, *J* 11.2 and 15.2 Hz, $CH_ACH_BCO_2$), 1.50—1.40 (1 H, m, C*H*Me), 0.98 (3 H, d, *J* 7.3 Hz, *Me*CH), and 0.28 (6 H, s, $SiMe_2$) (Found: M^+, 262.1407. $C_{15}H_{22}O_2Si$ requires *M*, 262.1389), *m*/*z* 262 (1.6%, M^+), 247 (45, *M* − Me), and 135 (100, $SiMe_2Ph$).

(4E)-(2RS,3SR)-*Allyl* 2-[(1SR)-1-*Dimethyl*(*phenyl*)*silylethyl*]-3-*hydroxyhex*-4-*enoate*.—Allyl 3-dimethyl(phenyl)silylbutyrate (1.83 g, 7 mmol) was treated successively with LDA (8 mmol) and crotonaldehyde, as described for the methyl ester above. Similar work-up and chromatography gave the β-*hydroxy ester* (1.07 g, 46%), as a viscous oil, R_F (hexane–EtOAc, 3:1, v/v) 0.33; $\nu_{max.}$(film) 3 460 (OH), 1 718 (CO), 1 242 (SiMe), and 1 105 cm^{-1} (SiPh); δ($CDCl_3$) 7.54—7.47 (2 H, m, ArH *ortho* to Si), 7.34—7.31 (3 H, m, ArH), 5.84 (1 H, m, OCH_2C*H*=CH_2), 5.59 (2 H, m, MeC*H*=C*H*), 5.28 (1 H, d, *J* 17.2 Hz, CH_AH_B=$CHCH_2O$), 5.20 (1 H, dd, *J* 10.4 and 1.1 Hz, CH_AH_B=$CHCH_2O$), 4.36 (2 H, m, OCH_2), 4.24 (1 H, t, *J* 6.7 Hz, C*H*OH), 2.66 (1 H, t, *J* 7.3 Hz, $CHCO_2$), 1.65 (3 H, d, *J* 5.1 Hz, *Me*CH=CH), 1.6 (1 H, br s, OH), 1.48 (1 H, quintet, *J* 7.5 Hz, CHSi), 1.00 (3 H, d, *J* 7.6 Hz, *Me*CHSi), and 0.31 and 0.29 (3 H, each, s, $SiMe_2$) (Found: *M* − Me, 317.1557. $C_{18}H_{25}O_3Si$ requires *M*, 317.1572); *m*/*z* 317 (1.5%, *M* − Me), 261 (17, *M* − C_4H_7O), and 135 (100, $SiMe_2Ph$).

(4E)-(2SR,3RS)-2-[(1RS)-1-*Dimethyl*(*phenyl*)*silylethyl*]-3-*hydroxyhex*-4-*enoic Acid* (**12**).—The allyl group was removed by the method of Ho.[20] Methyl-lithium (1.5M solution in ether; 6 mmol, 4 ml) was added slowly under nitrogen to copper(I) iodide (0.57 g, 3 mmol) in dry ether (5 ml) at −10 °C. The allyl ester (0.38 g, 1.14 mmol) in ether (1 ml) was added and left for 1 h at 0 °C, quenched with 3M hydrochloric acid (5 ml), further diluted with ether (10 ml) and filtered through Celite. The filtrate was extracted with aqueous sodium hydroxide (5%; 3 × 5 ml). Reacidification of the combined alkaline extracts gave a suspension of the acid, which was extracted with dichloromethane (3 × 15 ml), washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the *acid* (0.29 g, 88%) as a viscous oil, R_F (hexane–EtOAc, 3:1, v/v) 0.1 (streak); $\nu_{max.}$(CCl_4) 3 100 (br s, OH), 1 695 (CO), 1 245 (SiMe), and 1 105 cm^{-1} (SiPh); δ($CDCl_3$) 7.56 —7.48 (2 H, m, ArH *ortho* to Si), 7.36—7.31 (3 H, m, ArH), 5.70—5.53 (2 H, m, CH=CH), 4.25 (1 H, t, *J* 6.8 Hz, C*H*OH), 2.67 (1 H, t, *J* 7 Hz, $CHCO_2$), 1.66 (3 H, d, *J* 4.9 Hz, *Me*CH=CH), 1.48 (1 H, quintet, *J* 7.3 Hz, CHSi), 1.00 (3 H, d, *J* 7.6 Hz, *Me*CHSi), and 0.33 and 0.32 (3 H, each, s, $SiMe_2$) (Found: *M* − Me − H_2O, 259.1138. $C_{15}H_{19}O_2Si$ requires *M*, 259.1155); *m*/*z* 259 (1%, *M* − Me − H_2O), 143 (59, $PhMe_2SiCH_2$), and 135 (100, $SiMe_2Ph$).

(3Z,5E)-(*Hepta*-3,5-*dien*-2-*yl*)*dimethyl*(*phenyl*)*silane* (**10**).—Benzenesulphonyl chloride (2 mmol) was added to a solution of the β-hydroxy acid (1 mmol) in anhydrous pyridine (7 ml) at 0 °C. The mixture was shaken, sealed, and placed in the refrigerator for 18 h. It was then poured onto crushed ice and extracted several times with ether. The combined ether extracts were dried ($MgSO_4$), evaporated under reduced pressure, and the residue flash chromatographed, to give the dienes (**3**) and (**10**) (50%) in a ratio of 10:90 (^{1}H-n.m.r.); δ($CDCl_3$) [for the (3*Z*,5*E*)-isomer (**10**)] 7.5—7.3 (5 H, m, Ph), 6.17 (1 H, dd, *J* 11 and 14.7 Hz, MeCH=C*H*), 5.85 (1 H, t, *J* 11 Hz, MeCH=CHC*H*), 5.58 (1 H, dq, *J* 14.7 and 6.1 Hz, MeC*H*=CH), 5.06 (1 H, t, *J* 11 Hz, MeCHSiC*H*), 2.24 (1 H, dq, *J* 11 and 7.3 Hz, CHSi), 1.72 (3 H, dd, *J* 6.1 and 1.2 Hz, *Me*CH=CH), 1.00 (3 H, d, *J* 7.3 Hz, *Me*CHSi), and 0.26 (6 H, s, $SiMe_2$); *m*/*z* 230

(1.4%, M^+) and 135 (100, $SiMe_2Ph$) (Found M^+, 230.1509). In contrast to our normal observations,[10] the β-lactone in this series was not isolated, but had decomposed directly to the diene.

(4SR,5RS,8SR,9SR)-5-[(1RS)-1-*Dimethyl(phenyl)silylethyl*]-8-*methyl*-2-*phenyl*-4,5,8,9-*tetrahydroisoindole*-1,3-*dione* (**4**) *and* (4RS,5SR,8RS,9RS)-5-[(1RS)-1-*Dimethyl(phenyl)silylethyl*]-8-*methyl*-2-*phenyl*-4,5,8,9-*tetrahydroisoindole*-1,3-*dione* (**5**).—The diene (**3**) [0.72 g, of a 92:8 mixture of the (*E,E*) and (*E,Z*)-isomers, 3.13 mmol], *N*-phenylmaleimide (1.0 g, 5.8 mmol), and a crystal of hydroquinone were heated in benzene (25 ml) at 60 °C for 2 days under nitrogen. The solvent was then evaporated under reduced pressure and the residue flash chromatographed (SiO_2; hexane–EtOAc, 8:1, v/v) to give unchanged (*E,Z*)-dienylmethylsilane (**10**) (50 mg), the *major adduct* (**4**) (0.91 g, 79%); R_F (hexane–EtOAc, 5:1, v/v) 0.26; $\nu_{max.}$(film) 1 770 and 1 705 (CO), 1 250 (SiMe), and 1 110 cm^{-1} (SiPh); δ($CDCl_3$) 7.48—7.12 (10 H, m, 2 × Ph), 5.61 (2 H, m, CH=CH), 3.46 (1 H, dd, *J* 8.4 and 5.2 Hz, CHCO), 3.07 (1 H, t, *J* 8 Hz, CHCO), 2.46 (1 H, m, C*H*CH=CH), 2.28—2.18 (1 H, m, C*H*CH=CH), 1.87 (1 H, dq, *J* 12.3 and 7.3 Hz, CHSi), 1.43 (3 H, d, *J* 7.3 Hz, *Me*CHCH=), 1.20 (3 H, d, *J* 7.3 Hz, *Me*CHSi), and 0.33 (6 H, s, $SiMe_2$) (Found: M^+, 403.1944. $C_{25}H_{29}NO_2Si$ requires *M*, 403.1967); *m/z* 403 (1.5%, M^+), 308 (100, *M* − Me − Ph − 3H) and 135 (65, $SiMe_2Ph$), and the *minor adduct* (**5**) (0.19 g, 17%), R_F (hexane–EtOAc, 10:1, v/v) 0.32; $\nu_{max.}$(CCl_4) 1 775 and 1 710 (CO), 1 248 (SiMe), and 1 110 cm^{-1} (SiPh); δ($CDCl_3$) 7.52—7.08 (10 H, m, 2 × Ph), 5.97—5.66 (2 H, m, CH=CH), 3.15 (1 H, dd, *J* 8 and 5.5 Hz, CHCO), 2.99 (1 H, t, *J* 8 Hz, CHCO), 2.39 (1 H, m, C*H*CH=), 2.2 (1 H, m, C*H*CH=), 2.08 (1 H, dq, *J* 9.3 and 7.2 Hz, CHSi), 1.47 (3 H, d, *J* 7.1 Hz, *Me*CHCH=), 1.06 (3 H, d, *J* 7.1 Hz, *Me*CHSi), and 0.33 (6 H, s, $SiMe_2$) (Found: M^+, 403.1947. $C_{25}H_{29}NO_2Si$ requires *M*, 403.1967); *m/z* 403 (2%, M^+), 308 (100, *M* − Me − Ph − 3H), and 135 (60, $SiMe_2Ph$).

Diels–Alder Reaction of the Diene (**6**) *with* N-*Phenylmaleimide*.—Following Franck[1] we obtained the adducts (80%) in a ratio of 7.3:1, just as he and his co-workers did. Chromatography gave the major adduct (**8**) as needles, m.p. 129—130 °C (from hexane–EtOAc) (lit.,[1] m.p. 135 °C, lit.,[21] m.p. 130 °C) and the minor adduct (**7**) as a viscous oil (lit.,[1] gummy yellow mass) with spectra closely similar to those reported.

Hydrogenation of the Diels–Alder Adduct (**4**).—The adduct (**4**) (180 mg) was stirred with 10% palladium on charcoal (40 mg) in methanol (10 ml) under hydrogen at room temperature and pressure for 6 h. The catalyst was filtered off and the solvent evaporated off. Preparative t.l.c. (hexane–EtOAc, 5:1, v/v) gave (4SR,5RS,8SR,9SR) 5-[(1RS)-1-*dimethyl(phenyl)silylethyl*]-4,5,6,7,8,9-*hexahydro*-8-*methyl*-2-*phenylisoindole*-1,3-*dione* (162 mg, 90%); R_F (hexane–EtOAc, 5:1, v/v) 0.28; $\nu_{max.}$(CCl_4) 1 770 and 1 705 (C=O), 1 248 (SiMe) and 1 110 cm^{-1} (SiPh); δ($CDCl_3$) 7.53—7.19 (10 H, m, 2 × Ph), 3.40 (1 H, dd, *J* 8.4 and 4.5 Hz, CHCO), 3.01 (1 H, dd, *J* 8.4 and 6.1 Hz, CHCO), 2.2—1.2 (7 H, m, $CHCH_2CH_2CHCHSi$), 1.15 (3 H, d, *J* 7.2 Hz, *Me*CH), 1.14 (3 H, d, *J* 7 Hz, *Me*CH), and 0.31 and 0.29 (3 H, each, s, $SiMe_2$) (Found: M^+, 405.2132. $C_{25}H_{31}NO_2Si$ requires *M*, 405.2124); *m/z* 405 (4%, M^+) and 135 (100, $SiMe_2Ph$).

Hydrogenation of the Diels–Alder Adduct (**5**).—The adduct (**5**) (200 mg) was hydrogenated in the same way to give (4RS,5SR,8RS,9RS)-5-[(1RS)-1-*dimethyl(phenyl)silylethyl*]-4,5,6,7,8,9-*hexahydro*-8-*methyl*-2-*phenylisoindole*-1,3-*dione* (180 mg, 89%), R_F (hexane–EtOAc, 5:1, v/v), 0.34; $\nu_{max.}$(film) 1 770 and 1 700 (CO), 1 245 (SiMe), and 1 105 cm^{-1} (SiPh); δ($CDCl_3$) 7.55—7.14 (10 H, m, 2 × Ph), 2.93 and 2.84 (1 H each, m, 2 × CHCO), 2.25—1.2 (7 H, m, $CHCH_2CH_2$-CHCHSi), 1.12 (3 H, d, *J* 7 Hz, *Me*CH), 0.95 (3 H, d, *J* 7.2 Hz, *Me*CH), and 0.33 and 0.32 (3 H each, s, $SiMe_2$) (Found: M^+, 405.2130. $C_{25}H_{31}NO_2Si$ requires *M*, 405.2124); *m/z* 405 (5%, M^+) and 135 (100, $SiMe_2Ph$).

(4RS,5RS,8SR,9SR)-4,5,6,7,8,9-*Hexahydro*-5-[(1RS)-1-*hydroxyethyl*]-8-*methyl*-2-*phenylisoindole*-1,3-*dione* (**16**).—Mercuric acetate (115 mg, 0.36 mmol) was added to a stirred solution of the hydrogenated *imide* (122 mg, 0.3 mmol), derived from the major adduct (**4**), in peracetic acid (15% solution in acetic acid, containing 1% sulphuric acid; 3 ml) and the mixture kept at room temperature for 1 h and then at 35 °C for a further 2 h. The mixture was then added to a mixture of sodium acetate (100 mg), powdered sodium thiosulphate (1 g), and ether (20 ml) and stirred at room temperature for 1 h. This was then filtered through Celite and washed through with ethyl acetate (20 ml). The solvent was evaporated under reduced pressure and the residue dissolved in ethyl acetate (5 ml) and filtered through silica gel. The filtrate was evaporated under reduced pressure and the residue purified by preparative t.l.c. (SiO_2; hexane–EtOAc, 2:1, v/v) to give the *alcohol* (**16**) (60 mg, 70%), m.p. 82—83 °C (from hexane–EtOAc) (Found: C, 71.05; H, 7.65; N, 5.05. $C_{17}H_{21}NO_3$ requires C, 71.05; H, 7.36, and N, 4.87%); R_F (hexane–EtOAc, 2:1, v/v) 0.18; $\nu_{max.}$(CCl_4) 3 460 (OH) and 1 775 and 1 705 cm^{-1} (CO); δ($CDCl_3$) 7.66—7.21 (5 H, m, Ph), 4.25 (1 H, dq, *J* 2.7 and 6.4 Hz, MeC*H*OH), 3.87 (1 H, br s, OH), 3.21 (1 H, dd, *J* 8.6 and 4.7 Hz, CHCO), 3.14 (1 H, dd, *J* 8.6 and 6.1 Hz, CHCO), 2.34—1.34 (7 H, m, $CHCH_2CH_2CHCHO$), 1.29 (3 H, d, *J* 6.4 Hz, *Me*CHOH), and 1.15 (3 H, d, *J* 7 Hz, *Me*CH) (Found: M^+, 287.1518. $C_{17}H_{21}NO_3$ requires *M*. 287.1522); *m/z* 287 (14%, M^+) and 93 (100, $PhNH_2$).

(3RS,6RS,7SR,8SR,9SR)-3,6-*Dimethyl*-7-(N-*phenylamido*)-*hexahydrophthalide* (**17**).—The imide (105 mg, 0.25 mmol), derived from the hydrogenated minor adduct (**5**), was similarly converted into the *lactone* (**17**) (55 mg, 75%); it formed needles, m.p. 134—135 °C (from hexane–EtOAc) (Found: C, 71.1; H, 7.6; N, 4.87. $C_{17}H_{21}NO_3$ requires C, 71.1; H, 7.35, and N, 4.87%); R_F (hexane–EtOAc, 2:1, v/v) 0.24; $\nu_{max.}$(CH_2Cl_2) 3 450—3 150 (NH), 1 760 (lactone CO), 1 670 and 1 600 (amide CO), 1 550 (NH bend), 1 500, and 1 200 cm^{-1}; δ($CDCl_3$) 10.3—9.3 (1 H, br s, NH), 7.56 (2 H, d, *J* 8.1 Hz, ArH *ortho* to NHCO), 7.30 (2 H, dd, *J* 7.5 and 8.2 Hz, ArH *meta* to NHCO), 7.08 (1 H, dt, 0.9 and 7.4 Hz, ArH *para* to NHCO), 4.59 (1 H, br s, MeC*H*OH), 3.19 (1 H, t, *J* 6.6 Hz, CHCO), 2.94 (1 H, dd, *J* 5.4 and 4.8 Hz, CHCO), 2.35—1.50 (7 H, m, $CHCH_2CH_2CHCHO$), 1.39 (3 H, d, *J* 6.4 Hz, *Me*CHOH), and 1.06 (3 H, d, *J* 6.9 Hz, *Me*CH) (Found: M^+, 287.1523. $C_{17}H_{21}NO_3$ requires *M*, 287.1522); *m/z* 287 (20%, M^+) and 93 (100, $PhNH_2$). In using this reaction[12] as an example of the conversion of a phenyldimethylsilyl group into a hydroxy group, we drew the product as the alcohol instead of as the lactone; we thank Dr. Reitz for alerting us to this error.

Hydrogenation of the Adducts (**7**) *and* (**8**).—The adducts (**7**) and (**8**) were hydrogenated in the same way as the adducts (**4**) and (**5**). The major adduct (**8**) (300 mg) gave the *lactone* (**17**) (200 mg, 83%), identical (^{1}H-n.m.r.) with the compound described above, and the minor adduct (**7**) gave the alcohol (**16**) (75%), identical (^{1}H-n.m.r.) with the compound described above.

Diels–Alder Reaction between the Diene (**22**) *and Dimethyl Acetylenedicarboxylate*.—The diene alcohol (**22**) (0.56 g, 5 mmol), dimethyl acetylenedicarboxylate (DMAD) (0.86 g, 6 mmol), and a crystal of hydroquinone were refluxed in toluene (5 ml) for 2 days under nitrogen. The solvent was evaporated off

Table 1. Bond lengths (Å)

C(1)–C(2)	1.539(6)	C(2)–C(3)	1.505(6)
C(2)–O(1)	1.465(4)	C(3)–C(4)	1.518(5)
C(3)–C(8)	1.483(4)	C(4)–C(5)	1.543(7)
C(5)–C(6)	1.544(5)	C(6)–C(7)	1.511(5)
C(6)–C(12)	1.539(5)	C(7)–C(8)	1.345(5)
C(7)–C(10)	1.495(4)	C(8)–C(9)	1.481(5)
C(9)–O(1)	1.365(5)	C(9)–O(2)	1.190(4)
C(10)–O(3)	1.340(5)	C(10)–O(4)	1.187(6)
C(11)–O(3)	1.432(4)		

Table 2. Bond angles (°)

C(1)–C(2)–C(3)	117.1(3)	C(1)–C(2)–O(1)	105.7(3)
C(3)–C(2)–O(1)	104.6(3)	C(2)–C(3)–C(4)	118.4(3)
C(2)–C(3)–C(8)	100.4(2)	C(4)–C(3)–C(8)	111.0(3)
C(3)–C(4)–C(5)	107.3(3)	C(4)–C(5)–C(6)	112.3(3)
C(5)–C(6)–C(7)	111.7(3)	C(5)–C(6)–C(12)	114.0(3)
C(7)–C(6)–C(12)	109.7(3)	C(6)–C(7)–C(8)	121.3(3)
C(6)–C(7)–C(10)	117.2(3)	C(8)–C(7)–C(10)	121.5(3)
C(3)–C(8)–C(7)	125.4(3)	C(3)–C(8)–C(9)	107.6(3)
C(7)–C(8)–C(9)	126.4(3)	C(8)–C(9)–O(1)	107.1(2)
C(8)–C(9)–O(2)	130.9(4)	O(1)–C(9)–O(2)	122.0(4)
C(7)–C(10)–O(3)	111.6(4)	C(7)–C(10)–O(4)	122.9(3)
O(3)–C(10)–O(4)	125.4(3)	C(2)–O(1)–C(9)	109.3(3)
C(10)–O(3)–C(11)	116.7(3)		

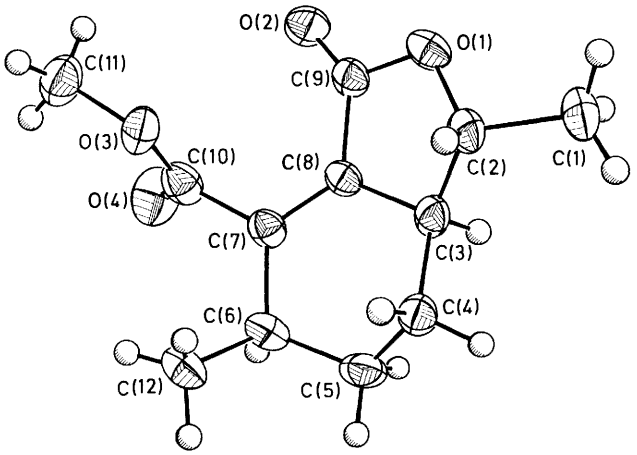


Figure. Molecular structure of the lactone (**26**) showing the atom numbering

and the residue flash chromatographed to give an inseparable mixture (2.7:1, ^{1}H n.m.r.) of the adducts[1] (**23**) and (**24**) (0.7 g, 55%); R_F (hexane–EtOAc, 2:1, v/v) 0.15; $\nu_{max.}$(film) 3 500br (OH), 1 720 (CO), 1 260 and 1 060 cm^{-1}; δ($CDCl_3$) 5.87 and 5.65 (1 H each, dd, *J* 10.2 and 4.4 Hz, CH=CH), 5.85 and 5.74 (1 H each, m, CH=CH for the minor isomer), 3.77 (6 H s, 2 × CO_2Me), 3.76 (6 H, s, 2 × CO_2Me for the minor isomer), 4.05—3.95 (1 H, m, C*H*OH), 3.35—3.14 (2 H, m, C*H*CH=CHC*H*), 2.05 (1 H, br s, OH), 1.22 (6 H, d, *J* 7.16 Hz, 2 × Me), and 1.16 (6 H, d, *J* 6.3 Hz, 2 × Me for the other isomer), together with a small amount of the corresponding aromatised phthalide, 7-*methoxycarbonyl*-3,6-*dimethylphthalide* (80 mg, 7%) R_F (hexane–EtOAc, 2:1, v/v) 0.22; $\nu_{max.}$(film) 1 760 and 1 730 cm^{-1} (CO); δ($CDCl_3$) 7.51 and 7.35 (1 H each, d, *J* 7.9 Hz, ArH), 5.50 (1 H, q, *J* 6.68 Hz, MeC*H*O), 4.00 (3 H, s, CO_2Me), 2.41 (3 H, s, *Me*Ar), and 1.60 (3 H, d, *J* 6.7 Hz, *Me*CHO) (Found: M^+, 220.0731. $C_{12}H_{12}O_4$ requires *M*, 220.0736); *m*/*z* 220 (9.2%, M^+), 205 (30, *M* − Me), 189 (45, *M* − OMe), and 188 (100, *M* − MeOH).

Table 3. Atomic co-ordinates (× 10^4)

	x	*y*	*z*
C(1)	2 116(5)	13 388(4)	5 553(5)
C(2)	2 781(4)	11 950(4)	4 458(4)
C(3)	1 565(4)	11 916(3)	3 640(4)
C(4)	1 656(5)	12 822(4)	2 018(4)
C(5)	633(5)	12 239(4)	1 289(5)
C(6)	1 483(5)	10 361(4)	986(4)
C(7)	2 190(4)	9 355(4)	2 302(4)
C(8)	2 099(4)	10 094(3)	3 529(4)
C(9)	2 782(4)	9 252(4)	4 864(4)
C(10)	2 975(5)	7 505(4)	2 193(5)
C(11)	5 572(5)	5 175(4)	1 973(6)
C(12)	2 923(5)	9 956(4)	−631(5)
O(1)	3 009(3)	10 425(3)	5 497(3)
O(2)	3 080(3)	7 850(3)	5 399(3)
O(3)	4 695(3)	6 944(2)	1 992(3)
O(4)	2 161(4)	6 674(3)	2 212(5)

Dimethyl (3SR,6RS)-3,6-*Dihydro*-3-[(1RS)-1-*dimethyl*-(*phenyl*)*silylethyl*]-6-*methylphthalate* (**25**).—The diene (**3**) [92:8 mixture of (*E*,*E*) and (*E*,*Z*)-isomers; 220 mg, 0.95 mmol], DMAD (300 mg, 2.1 mmol), and a crystal of hydroquinone were refluxed in toluene (5 ml) for 2 days under nitrogen. The solvent was evaporated off and the residue flash chromatographed to give unchanged dienylmethylsilane [3:1 mixture of (*E*,*E*) and (*E*,*Z*) isomers, 70 mg, 31%] and the *adduct* (**25**) [200 mg, 62% based on (*E*,*E*)-diene not recovered]; R_F (hexane–EtOAc, 5:1, v/v) 0.29; $\nu_{max.}$(CCl_4) 1 725 (CO) and 1 110 cm^{-1} (SiPh); δ($CDCl_3$) 7.53—7.33 (5 H, m, Ph), 5.64 (1 H, ddd, *J* 10.1, 4.1 and 1.2 Hz, C*H*=CH), 5.34 (1 H, ddd, *J* 10.1, 4 and 1 Hz, CH=C*H*), 3.74 and 3.73 (3 H each, s, 2 × CO_2Me), 3.37 (1 H, m, C*H*CHSi), 3.08 (1 H, m, MeC*H*CH=), 1.34 (1 H, dq, *J* 2.8 and 7.5 Hz, CHSi), 1.19 (3 H, d, *J* 7.1 Hz, *Me*CH), 0.86 (3 H, d, *J* 7.5 Hz, *Me*CHSi), and 0.34 and 0.31 (3 H, s, $SiMe_2$) (Found: M^+, 372.1749. $C_{21}H_{28}O_4Si$ requires *M*, 372.1757); *m*/*z* 372 (2.7%, M^+), 163 [69, *M*, − (2 × Me − CO_2 − $SiMe_2Ph$)], and 135 (100, $SiMe_2Ph$).

Hydrogenation of the Adduct (**25**).—The adduct (**25**) (170 mg, 0.45 mmol) was hydrogenated, as described above for the adduct (**4**), to give *dimethyl* (3SR,4RS)-3-[(1RS)-1-*dimethyl*-(*phenyl*)*silylethyl*]-6-*methyl*-3,4,5,6-*tetrahydrophthalate* (150 mg, 88%); R_F (hexane–EtOAc, 5:1, v/v) 0.29; $\nu_{max.}$(film) 1 725 (CO) and 1 110 cm^{-1} (SiPh); δ($CDCl_3$) 7.50—7.32 (5 H, m, Ph), 3.75 and 3.70 (3 H each s, 2 × CO_2Me), 2.75 and 2.55 (1 H each, m, MeC*H*CH_2 and C*H*CHSi), 1.60—1.17 (5 H, m, CH_2CH_2 and CHSi), 1.14 (3 H, d, *J* 6.9 Hz, *Me*CH), 0.93 (3 H, d, *J* 7.3 Hz, *Me*CHSi), and 0.32 and 0.29 (3 each, s, $SiMe_2$) (Found: M^+, 374.1919. $C_{21}H_{30}O_4Si$ requires *M*, 374.1924); *m*/*z* 374 (13.4%, M^+), 179 (66, $SiMe_2Ph$ − CO_2 − CH_4), and 135 (100, $SiMe_2Ph$).

(3SR,6RS,9SR)-7-*Methoxycarbonyl*-3,6-*dimethyl*-4,5,6,9-*tetrahydrophthalide* (**26**).—The diester (69 mg, 0.18 mmol), derived from the hydrogenated adduct (**25**), was converted into the corresponding alcohol using mercuric acetate and peracetic acid, as described for the preparation of the alcohol (**16**). Lactonisation spontaneously took place in the acidic medium to give the lactone (30 mg, 73%) as needles, m.p. 94—95 °C (lit.,[1] m.p. 97 °C); R_F (hexane–EtOAc, 2:1, v/v) 0.31, with spectra; $\nu_{max.}$(CCl_4) 1 760 and 1 730 cm^{-1} (C=O); δ($CDCl_3$) 4.13 (1 H, dq, *J* 9.16 and 6.15 Hz, MeC*H*O), 3.82 (3 H, s, CO_2Me), 2.79 and 2.45 (1 H each, m, MeC*H* and C*H*CHO, 1.92—1.71 and 1.30—1.15 (4 H, m, CH_2CH_2), 1.48 (3 H, d, *J* 6.1 Hz, *Me*CHO), and 1.08 (3 H, d, *J* 7.2 Hz, *Me*CH) (Found:

M^+, 224.1055. $C_{12}H_{16}O_4$ requires M, 224.1049); m/z 224 (5.8%, M^+), 180 (78, $M - CO_2$), and 165 (100, $M - CO_2Me$) similar to those reported.[1] The structure was confirmed by single crystal X-ray crystallography taken on colourless prisms obtained from hexane–ethyl acetate solution by slow cooling. The result is illustrated in the Figure.

Crystal Data.—$C_{12}H_{16}O_4$, M = 224.26, triclinic, a = 8.722(2), b = 8.706(2), c = 9.024(2) Å, α = 79.29(2), β = 69.01(2), γ = 67.35(1)°, V = 589.5 Å^3 (by least-squares refinement on diffractometer angles for 21 automatically centred reflections, λ = 1.541 78 Å), space group $P\bar{1}$ (No. 2), Z = 2, D_x = 1.26 g cm^{-3}, $F(000)$ = 240. Colourless prisms. Crystal dimensions: 0.20 × 0.32 × 0.32 mm, μ(Cu-K_α) = 7.43 cm^{-1}.

Data Collection and Processing.—Nicolet $R3m\mu$ diffractometer, $\omega/2\theta$ scan mode, scan range from 1.0° below K_{α_1} to 1.0° above K_{α_2}, scan speed 2.93—29.30°/min, graphite-monochromated Cu-K_α radiation; 3 328 reflections measured ($5.0 \leqq 2\theta \leqq 116.0°$, $\pm h$, $\pm k$, $\pm l$), 1 609 unique [merging R = 0.043 after empirical absorption correction based on an ellipsoid model and azimuthal scan data from 10 independent reflections (max., min. transmission factors = 0.628, 0.306)], giving 1 472 with $F > 4\sigma(F)$. Approximately linear crystal decay, *ca.* 22%, corrected during processing.

Structure Analysis and Refinement.—Direct methods followed by Fourier difference synthesis for all non-hydrogen atoms. Blocked-cascade least-squares refinement based on F. Non-hydrogen atoms refined with anisotropic thermal parameters, hydrogens riding on C with C–H = 0.96 Å and separate isotropic U's for different H-types. The weighting scheme $w^{-1} = [\sigma^2(F) + 0.0007F^2]$, with $\sigma(F)$, from counting statistics gave satisfactory agreement analyses. Final R and R_w values for 148 parameters are 0.089, 0.107; the high values of the residuals were attributed to crystal decay during data collection. A final Fourier difference map revealed no regions of electron density greater than 0.48 eÅ^{-3}.

The final atomic co-ordinates are presented in Tables 1—3. Complex neutral scattering factors were employed throughout,[22] and calculations were performed on a Desktop Data General Eclipse computer using the SHELXTL package.[23]

The Lactones (**26**) *and* (**27**) *prepared from the Adducts* (**24**) *and* (**25**).—The mixture of adducts (**23**) and (**24**) was hydrogenated as before and the crude products were stirred at room temperature with a catalytic amount of toluene-*p*-sulphonic acid in the methanol for 24 h. Work-up and preparative t.l.c. (SiO_2; hexane–EtOAc, 2:1, v/v) gave the lactone (**26**) (18%), identical (t.l.c., m.p., i.r., ^{1}H n.m.r.) to the compound prepared earlier, and the lactone (**27**) (50%) as needles, m.p. 74—75 °C (from hexane–EtOAc) (lit.,[1] m.p. 76 °C); R_F (hexane–EtOAc, 2:1, v/v) 0.27; $\nu_{max.}$(CCl_4) 1 755 and 1 725 cm^{-1} (C=O); δ($CDCl_3$) 4.83 (1 H, dq, J 8.3 and 6.5 Hz, MeC*H*O), 3.82 (3 H, s, CO_2Me), 3.04 and 2.79 (1 H each, m, C*H*CHO and MeC*H*), 1.85—1.30 (4 H, m, CH_2CH_2), 1.21 (3 H, d, J 6.5 Hz, *Me*CHO), and 1.10 (3 H, d, J 7.2 Hz, *Me*CH) (Found: M^+, 224.1057. $C_{12}H_{16}O_4$ requires M, 224.1048); m/z 224 (8%, M^+), 180 (47, $M - CO_2$), and 165 (100, $M - CO_2Me$), similar to the spectra reported.[1]

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