

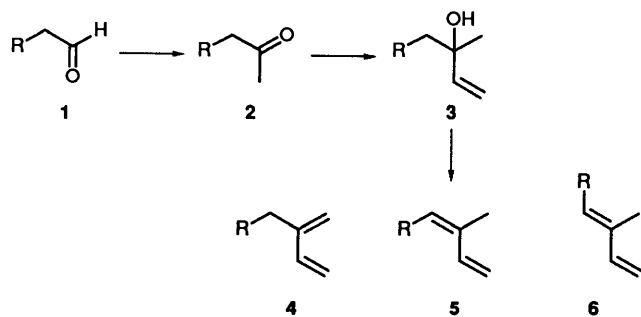
Silicon-Directed Diene Synthesis

Paul A. Brown, Roger V. Bonnert, Paul R. Jenkins,* Nicholas J. Lawrence and Mohammed R. Selim

Department of Chemistry, The University, Leicester, LE1 7RH, UK

A synthesis of 2-substituted-1,3-dienes is reported which uses silicon as a control element: Eight aldehydes were converted into α -silyl ketones by treatment with trimethylsilylmethylmagnesium chloride and rapid Collins oxidation. Addition of vinylmagnesium bromide to the resulting α -silyl ketones, followed by Peterson elimination, gave a series of dienes. The route was used to make (4*S*)-3-methylene-t-[(phenylmethoxy)methoxy]pent-1-ene from (-)-ethyl lactate; low asymmetric induction was observed in the Diels–Alder reactions of this diene with diethyl fumarate and *N*-phenylmaleimide.

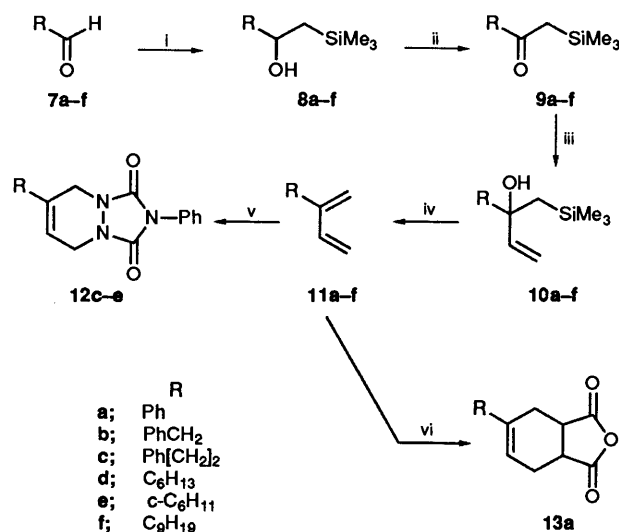
Our synthetic programme on the taxane natural products¹ required a reliable method for the conversion of an aldehyde into a 2-substituted-1,3-diene. Initial studies were based on a sequence in which the aldehyde **1** (Scheme 1) was treated with methylmagnesium bromide and the resulting alcohol was then oxidised to the ketone **2**. Subsequent reaction with vinylmagnesium bromide produced the tertiary allylic alcohol **3**, treatment of which with acid leads to the initial formation of a tertiary allylic carbocation which loses one of three possible protons to give the three dienes **4–6**. The elegant studies of Fleming² have shown that silicon acts as an effective control element in this situation since nucleophilic attack at silicon is much faster than attack at a proton. Hence modification of the route outlined in Scheme 1 to introduce a strategic silyl group would be expected to lead to the regiocontrolled synthesis of a single diene instead of a mixture. Previous work in this area has shown that the Peterson elimination may be used to synthesize 1-trimethylsilylbuta-1,3-diene³ and other 1,3-dienes;⁴ however, to the best of our knowledge, this is the first time that a trimethylsilyl group causes double-bond formation in one arm of a branching carbon framework leading to a single diene. We now report in full an effective route for the conversion of a range of aldehydes into 2-substituted-1,3-dienes.



Scheme 1

Results and Discussion

The route outlined in Scheme 2 is described in detail for example **a** where R = Ph (the yields for all six examples are shown in Table 1). Benzaldehyde **7a** combined with trimethylsilylmethylmagnesium chloride to produce the silyl alcohol **8a** in 97% yield. Rapid Collins oxidation⁵ with a reaction time of 1 min gave the silyl ketone **9a** (94%). The length of reaction was important as longer reaction times resulted in desilylation of the product. We attempted to use a shorter procedure which has previously been reported by Akiba and co-workers⁶ and which involves reaction of the Grignard reagent with an acyl chloride to produce an



Scheme 2 Reagents: i, $\text{Me}_3\text{SiCH}_2\text{MgCl}$; ii, CrO_3 -pyridine; iii, $\text{CH}_2=\text{CHMgBr}$; iv, AcOH, AcONa; v, 4-Ph-1,2,4-triazole-3,5-dione; vi, maleic anhydride

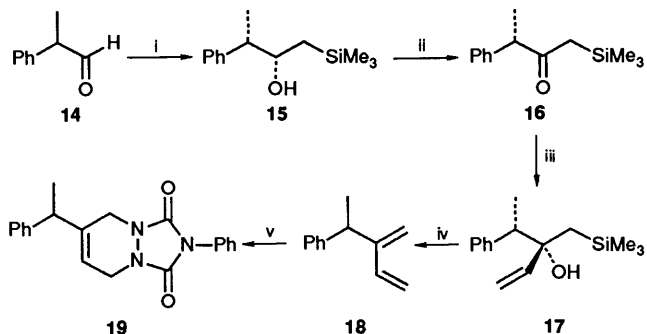
Table 1 Percentage yields of products **8–13**

Aldehyde 7 RCHO	8	9	10	11	12 (or 13)
a; PhCHO	97	94	95	65	70 (13)
b; PhCH ₂ CHO	90	86	88	50	
c; Ph(CH ₂) ₂ CHO	91	97	78	73	72 (12)
d; C ₆ H ₁₃ CHO	90	95	94	70	77 (12)
e; <i>c</i> -C ₆ H ₁₁ CHO	85	93	84	60	76 (12)
f; C ₉ H ₁₉ CHO	88	98	74	84	

α -silyl ketone, but in our hands it was less efficient than the procedure described above (Oertle⁷ has used this method in conjunction with our diene synthesis to make the aggregation pheromone ipsenol). Ketone **9a** was next treated with vinylmagnesium bromide to give the tertiary allylic alcohol **10a** (95%) which has the silyl group in the correct position for elimination to a 1,3-diene. In some cases the allylic alcohol was contaminated with traces of the starting ketone, but this did not affect the consequent reactions. The Peterson elimination⁸ went according to plan; treatment of the alcohol **10a** with acetic acid and sodium acetate gave a single diene **11a**. Maleic anhydride reacted with diene **11a** to produce a crystalline Diels–Alder

derivative **13a** (70%). In three other cases crystalline products were obtained from the Diels–Alder reaction with 4-phenyl-1,2,4-triazole-3,5-dione (Cookson's dieneophile).⁹ That the route is simple and clean was shown by the synthesis of the diene **11f**, obtained from the aldehyde **7f** in 52% yield without purification of any intermediate.

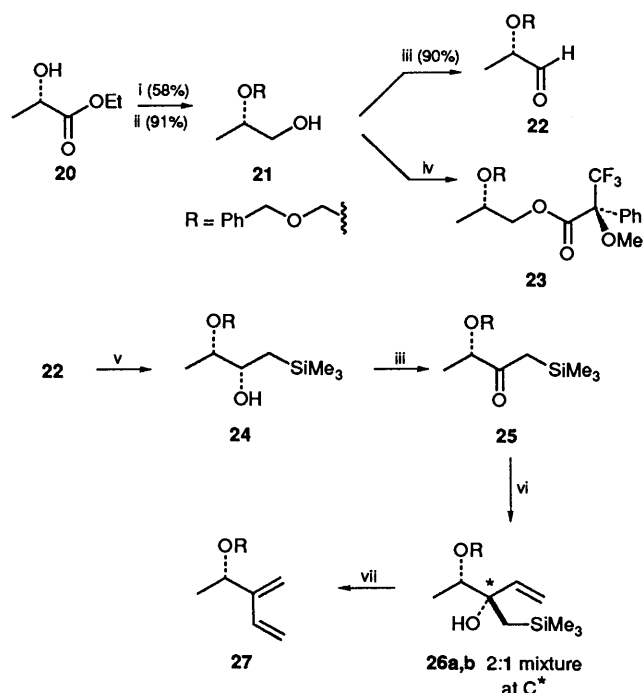
We next investigated the preparation of a chiral substituted diene, in racemic form, and its subsequent Diels–Alder reactions. 2-Phenylpropionaldehyde **14** (Scheme 3) reacted



Scheme 3 Reagents: as for Scheme 2

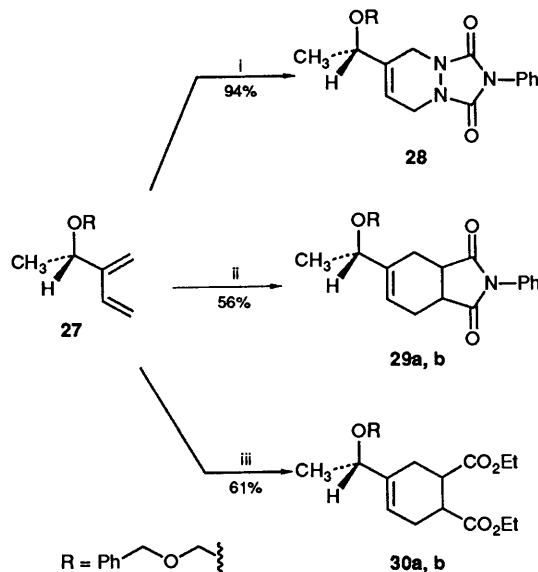
with trimethylsilylmethylmagnesium chloride to give a single diastereoisomer of the alcohol **15** (96%). It was not possible to obtain a crystalline derivative of this compound so the relative configurations of the two chiral centres were assigned using Cram's rule,¹⁰ which holds well for a number of examples of stereoselective addition to compound **14**.¹¹ It is worthy of note that the diastereoselectivity observed here with the silylated nucleophile is remarkably high when compared with the Cram:anti-Cram ratios observed in the addition of MeMgBr (66:34),^{10a} MeZnX (60:40),^{11f} MeCdX (60:40),^{11f} MeLi (75:25),^{11a} PhMgBr (>80:20),^{10a} MeTiCl₃ (90:10)^{11a} and ^tBuMgCl (very high)^{11g} to the same aldehyde **14**. Oxidation of the alcohol **15** by the Collins procedure (to the ketone **16**) and reaction with vinylmagnesium bromide furnished the tertiary allylic alcohol **17** as a single diastereoisomer which once again was assigned on the basis of Cram's rule. This assignment is in agreement with the observed stereoselectivity of additions to similar phenylethyl ketones.¹² The stereochemical assignment of alcohols **15** and **17** is, of course, of little importance here since one of the stereogenic centres in each case is destroyed, as in the Peterson elimination from the silyl alcohol **17** which gave the racemic diene **18** (73%), which in turn reacted with Cookson's dieneophile to give the Diels–Alder adduct **19**.

Finally, the methodology was applied to the synthesis of a homochiral 1,3-diene derived from the aldehyde **22** (Scheme 4). (–)-Ethyl lactate **20** was converted into aldehyde **22** in a standard series of reactions¹³ consisting of protection, as the benzyloxymethyl ether, reduction (lithium aluminium hydride) to give the alcohol **21** (we were unable to determine the optical purity at this stage since the Mosher ester **23** and that derived from racemic ethyl lactate gave no NMR signals that were suitably resolved), and finally oxidation to furnish the aldehyde **22**. The aldehyde **22** was of high optical purity (86%) by comparison with the known $[\alpha]_D^{20}$ -value.* Addition of trimethylsilylmethylmagnesium chloride to the aldehyde **22** gave a single diastereoisomer of the alcohol **24** from which we were unable to obtain a suitable crystalline derivative for X-ray analysis; hence the configuration was assigned, yet again, by applying Cram's rule; a 4:1 selectivity in this sense was observed, by



Scheme 4 Reagents: i, PhCH₂OCH₂Cl, Pr^t₂NEt; ii, LiAlH₄; iii, CrO₃·pyridine; iv, 1,3-dicyclohexylcarbodiimide (DCC), 2-methoxy-2-phenyl-3,3,3-trifluoropropionic acid, DMAP; v, Me₃SiCH₂MgCl; vi, vinylmagnesium bromide; vii, AcOH, AcONa

Burke *et al.*,¹⁴ in the addition of prop-2-enylmagnesium bromide to the same aldehyde **22**. Oxidation of the alcohol **24** to the ketone **25**, followed by addition of vinylmagnesium bromide, gave the alcohols **26a** and **26b**, this time as 2:1 mixture of diastereoisomers. The Peterson elimination of this mixture of compounds **26a** and **26b** afforded the homochiral 1,3-diene **27** (71%), which gave a Diels–Alder adduct **28** (94%) with Cookson's dieneophile. We are confident that the optical purity of the diene **27** is high, since when a (menthoxy)methoxy group¹⁵ was used in place of the (benzyloxy)methoxy group a diene of 91% diastereoisomeric esters (d.e.) was obtained.¹⁶ Reaction of the diene **27** with *N*-phenylmaleimide gave an adduct **29a** and **29b** (56%) which was a 1:1.28 mixture of



Scheme 5 Reagents and conditions: i, 4-phenyl-1,2,4-triazole-3,5-dione, 25 °C; ii, *N*-phenylmaleimide, toluene, reflux, 4 h; iii, diethyl fumarate, toluene, reflux, 4 h

* Optical rotation for compound **22**: $[\alpha]_D^{20} -22.7^\circ$ (*c* 2.3 in THF) {lit.,^{13a} $[\alpha]_D^{25} -26.5^\circ$ (*c* 1.5 in THF)}.

stereoisomers, whereas diethyl fumarate gave adducts **30a** and **30b** (61%) as a 1:1.3 mixture (Scheme 5).

Many examples of Diels–Alder reactions of dienes bearing chiral substituents are known but in all cases the chiral group is positioned at the terminal carbon of the diene.¹⁷ In some cases a high degree of diastereoselectivity was observed. The results described above are markedly less selective than the reported examples for 1-substituted-1,3-dienes. Although we have only a small number of examples, the lack of selectivity may be ascribed to the fact that the chiral group is not directly attached to the carbon undergoing bond formation, hence its stereochemical influence is reduced.

In conclusion we have developed a reliable method for the synthesis of dienes, which is based on the use of silicon as a control element.

Experimental

90 MHz ¹H NMR spectra were recorded on a Varian EM-390 spectrometer. High-field ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bucker AM-400 spectrometer in the highfield NMR service at the University of Warwick. NMR *J*-values are in Hz. Mass spectra were recorded on a V.G. micromass 16B spectrometer. Elemental analysis was carried out by CHN Analysis, Wigston, Leicester. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. M.p.s were determined on a Kofler hot-stage and are uncorrected.

Flash chromatography was carried out according to the method of Still *et al.*¹⁸ by using silica gel manufactured by Merck and Co., Kiesel 60, 230–400 mesh (ASTM). TLC was conducted on precoated aluminium sheets (60–254) with a 0.2 mm silica gel layer thickness, manufactured by Merck and Co.

Light petroleum refers to the 40–60 °C fraction; both light petroleum and ethyl acetate were distilled prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium metal in the presence of benzophenone. Ether refers to diethyl ether, which was distilled from LiAlH₄.

Unless specified as otherwise, standard aq. work-up involved addition of aq. ammonium chloride and extraction with ether (× 3). The extracts were dried (Na₂SO₄), and evaporated under reduced pressure.

1-Phenyl-2-(trimethylsilyl)ethanol 8a.—To a solution of benzaldehyde (1.5 g, 14.1 mmol) in ether (15 cm³) was added trimethylsilylmethylmagnesium chloride (14.1 cm³ of a 1.3 mol dm⁻³ solution in ether, 18.3 mmol) at room temperature under nitrogen. The mixture was heated under reflux for 1.5 h and, after cooling, standard aq. work-up and distillation gave the alcohol **8a**¹⁹ (2.56 g, 97%) as an oil, b.p. 100–103 °C/2 mmHg (lit.,¹⁹ 103–104 °C/3 mmHg); *R*_f 0.20 [ether–light petroleum (1:9, v/v)]; *v*_{max}(film)/cm⁻¹ 3300–3500s (br, OH), 2940s, 1250s, 1000s and 855s; *δ*_H(300 MHz; CDCl₃, pyrazine as standard) –0.06 (9 H, s, Me₃Si), 1.21 (1 H, dd, *J* 14 and 7, CHaHbSi), 1.30 (1 H, dd, *J* 14 and 7, CHaHbSi), 1.59 (1 H, br s, OH), 4.85 (1 H, t, *J* 7, CHOH) and 7.27–7.38 (5 H, m, ArH); *δ*_C(75 MHz; CDCl₃) 0.00 (q, Me₃Si), 28.54 (t), 72.9 (d), 125.78 (d), 127.51 (d), 128.46 (d) and 146.59 (s); *m/z* 193 (6%, M⁺ – 1) and 73 (100, SiMe₃).

1-Phenyl-3-(trimethylsilyl)propan-2-ol 8b.—In the same way phenylacetaldehyde **7b** (2.5 g, 20.8 mmol) and trimethylsilylmethylmagnesium chloride (20.8 cm³ of a 1.3 mol dm⁻³ solution in ether, 27.0 mmol) gave the alcohol **8b**¹⁹ (3.90 g, 90%) as an oil; *R*_f 0.40 [ether–light petroleum (1:9, v/v)]; b.p. 160–163 °C/0.5 mmHg (lit.,¹⁹ 62 °C/0.17 mmHg) (Found: C, 69.0; H, 9.5. Calc. for C₁₂H₂₀OSi: C, 69.16; H, 9.67%); *v*_{max}(film)/cm⁻¹ 3550–3200m (br, OH), 2975s, 1250s, 1080s and 860; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.084 (9 H, s, Me₃Si), 0.91 (1 H, d, *J*

6.1, CH^aH^bSi), 0.94 (1 H, d, *J* 7.7, CH^aH^bSi), 1.48 (1 H, br s, OH), 2.65 (1 H, dd, *J* 15.5 and 8.5, PhCH^aH^b), 2.87 (1 H, dd, *J* 15.50 and 3.70, PhCH^aH^b), 3.95–4.04 (1 H, m, CHOH) and 7.20–7.36 (5 H, m, ArH); *δ*_C (75 MHz; CDCl₃) –0.69 (q), 25.95 (t), 47.60 (t), 70.84 (d), 128.39 (d), 129.0 (d), 129.39 (d) and 138.85 (s); *m/z* 208 (7%, M⁺), 117 (90, M – H₂O – SiMe₃) and 73 (100, SiMe₃).

4-Phenyl-1-(trimethylsilyl)butan-2-ol 8c.—In the same way hydrocinnamaldehyde **7c** (2.7 g, 20.14 mmol) and trimethylsilylmethylmagnesium chloride (21.7 cm³ of a 1.3 mol dm⁻³ solution in ether, 28.19 mmol) gave the alcohol **8c** (4.06 g, 91%) as an oil, b.p. 120–123 °C/0.4 mmHg (Found: C, 70.3; H, 9.85. C₁₃H₂₂OSi requires C, 70.21; H, 9.97%); *R*_f 0.26 [ether–light petroleum (1:9, v/v)]; *v*_{max}(film)/cm⁻¹ 3500–3250m (br, OH), 1250s, 1030s, 840s and 700s; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.05 (9 H, s, Me₃Si), 0.92 (1 H, d, *J* 7.5, CHaHbSi), 0.95 (1 H, d, *J* 7.5, CHaHbSi), 1.37 (1 H, br s, OH), 1.70–1.94 (2 H, m, PhCH₂CH₂), 2.63–2.97 (2 H, m, PhCH₂), 3.84 (1 H, m, CHOH) and 7.16–7.33 (5 H, m, ArH); *δ*_C(75 MHz; CDCl₃) –0.70 (q, Me₃Si), 26.81 (t), 32.22 (t), 42.40 (t), 69.54 (d), 125.50 (d), 128.33 (d) and 142.18 (s); *m/z* 222 (5%, M⁺) and 91 (100, PhCH₂).

1-Trimethylsilyloctan-2-ol 8d.—In the same way heptaldehyde **7d** (3 g, 26.3 mmol) and trimethylsilylmethylmagnesium chloride (26.3 cm³ of a 1.3 mol dm⁻³ solution in ether, 34.1 mmol) gave the alcohol **8d**¹⁹ (4.7 g, 90%) as an oil, b.p. 105–108 °C/0.5 mmHg (lit.,¹⁹ 156–168 °C); *R*_f 0.58 [ether–light petroleum (1:5, v/v)]; *v*_{max}(film)/cm⁻¹ 3600–3200s (br, OH), 2850s, 1465s, 1250s and 840; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.03 (9 H, s, Me₃Si), 0.81–0.89 (5 H, m, CH₂Si and Me), 1.27–1.48 (11 H, m, 5 × CH₂ and OH) and 3.73–3.79 (1 H, m, CHOH); *δ*_C(75 MHz; CDCl₃) –0.68 (q), 14.02 (q), 22.60 (t), 25.75 (t), 26.76 (t), 29.30 (t), 31.88 (t), 40.90 (t) and 70.13 (d); *m/z* 202 (0.1%, M⁺), 184 (6, M – H₂O) and 73 (100, SiMe₃).

1-Cyclohexyl-2-(trimethylsilyl)ethanol 8e.—In the same way cyclohexanecarbaldehyde **7e** (2.5 g, 22.3 mmol) and trimethylsilylmethylmagnesium chloride (22.3 cm³ of a 1.3 mol dm⁻³ solution in ether, 28.99 mmol) gave the alcohol **8e**⁵ (4.20 g, 85%) as an oil, *R*_f 0.61 [ether–light petroleum (1:5, v/v)]; b.p. 95–98 °C/2 mmHg (lit.,⁵ 120 °C/0.5 mmHg) (Found: C, 66.0; H, 11.9. C₁₁H₂₄OSi requires C, 65.92; H, 12.07%); *v*_{max}(film)/cm⁻¹ 3600–3300m (br, OH), 1250s and 860s; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.03 (9 H, s, Me₃Si), 0.72 (1 H, dd, *J* 14.6 and 9.45, CHaHbSi), 0.83 (1 H, dd, *J* 14.6 and 4.6, CHaHbSi), 0.88–1.88 (12 H, m, C₆H₁₁ and OH) and 3.54 (1 H, quint, *J* 4.6, CHOH); *δ*_C(75 MHz; CDCl₃) –0.73 (q), 22.78 (t), 26.24 (t), 26.43 (t), 26.63 (t), 27.45 (t), 29.45 (t), 46.32 (d) and 74.25 (d); *m/z* 182 (3%, M – H₂O) and 73 (100, SiMe₃).

1-(Trimethylsilyl)undecan-2-ol 8f.—In the same way undecanal **7f** (1 g, 6.3 mmol) and trimethylsilylmethylmagnesium chloride (4.8 cm³ of a 1.6 mol dm⁻³ solution in ether, 7.7 mmol) gave the alcohol **8f** (1.35 g, 88%) as an oil, b.p. 100–104 °C/1 mmHg; *v*_{max}(film)/cm⁻¹ 3460br (OH), 2960s, 2940s, 2860s, 1255s and 865s; *δ*_H(90 MHz; CDCl₃) 0.06 (9 H, s, SiMe₃), 0.84–1.00 (5 H, m, SiCH₂ and CH₂Me), 1.30–1.86 (17 H, m, [CH₂]₈ and OH) and 3.60–3.93 (1 H, m, CHOH).

1-Phenyl-2-(trimethylsilyl)ethanone 9a.—To a stirred solution of pyridine (7.7 g, 91.6 mmol) in dry dichloromethane (100 cm³) was added chromium(vi) oxide (7.56 g, 76.4 mmol). An exothermic reaction occurred and the mixture became deep red during 30 min. A solution of the alcohol **8a** (2.2 g, 11.3 mmol) in dichloromethane (10 cm³) was added in one portion. The solution became brown immediately and TLC showed no

starting material. The mixture was then filtered through a short silica column and the residues were washed with ether (3 × 100 cm³). Removal of the solvent, under reduced pressure, and distillation gave the ketone **9a**²⁰ (2.05 g, 94%) as a yellow oil, b.p. 110–112 °C/8 mmHg (lit.²⁰ 47–50 °C/0.15 mmHg); *R*_f 0.33 [ether–light petroleum (1:9, v/v)] (Found: C, 68.9; H, 8.3. Calc. for C₁₁H₁₆O_{Si}: C, 68.69; H, 8.31%); *v*_{max}(film)/cm⁻¹ 1660s (CO), 1595m, 1580m, 1270s and 850s; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.08 (9 H, s, Me₃Si), 2.76 (2 H, s, CH₂Si) and 7.42–7.92 (5 H, m, ArH); *δ*_C(75 MHz; CDCl₃) –0.99 (q), 33.57 (t), 128.19 (d), 128.32 (d), 132.40 (d), 138.33 (s) and 199.32 (s, CO); *m/z* 192 (50%, M⁺), 177 (57, M – Me), 77 (50, Ph) and 73 (100, Me₃Si).

1-Phenyl-3-(trimethylsilyl)propan-2-one **9b**.—In the same way the alcohol **8b** (3.2 g, 15 mmol) gave the ketone **9b**²¹ (2.65 g, 86%) as a yellow oil, b.p. 130–133 °C/0.5 mmHg; *R*_f 0.25 [ether–light petroleum (1:9, v/v)]; *v*_{max}(film)/cm⁻¹ 1690s (CO), 1450s, 1250s, 1100s and 850s; *δ*_H(90 MHz; CDCl₃, pyrazine standard) 0.13 (9 H, s, Me₃Si), 2.27 (2 H, s, CH₂Si), 3.65 (2 H, s, PhCH₂) and 7.13–7.50 (5 H, m, ArH); *m/z* 206 (100%, M⁺), 115 (46, M – H₂O – SiMe₃) and 73 (54, SiMe₃).

4-Phenyl-1-(trimethylsilyl)butan-2-one **9c**.—In the same way the alcohol **8c** (3.5 g, 15.76 mmol) gave the ketone **9c** (3.36 g, 97%) as a yellow oil, b.p. 160–162 °C/0.4 mmHg; (Found: C, 70.85; H, 9.1. C₁₃H₂₀O_{Si} requires C, 70.80; H, 9.14%); *R*_f 0.58 [ether–light petroleum (1:9, v/v)]; *v*_{max}(film)/cm⁻¹ 1690m (CO), 1580s, 1430s, 1250s, 1030s, 850s and 700s; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.08 (9 H, s, Me₃Si), 2.22 (2 H, s, CH₂Si), 2.67 (2 H, t, *J* 7.9, PhCH₂CH₂), 2.88 (2 H, t, *J* 7.9 PhCH₂) and 7.15–7.31 (6 H, should be 5 H, ArH); *δ*_C(75 MHz; CDCl₃) –1.13 (q), 29.99 (t), 38.28 (t), 46.00 (t), 125.93 (d), 128.35 (d), 141.36 (s) and 207.96 (s, C=O); *m/z* 220 (100%, M⁺) and 91 (95, PhCH₂).

1-(Trimethylsilyl)octan-2-one **9d**.—In the same way the alcohol **8d** (4 g, 19.8 mmol) gave the ketone **9d** (3.7 g, 95%) as a purple oil, b.p. 125–127 °C/0.8 mmHg; *R*_f 0.72 [ether–light petroleum (1:5, v/v)]; *v*_{max}(film)/cm⁻¹ 1690s (CO); *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.05 (9 H, s, Me₃Si), 0.81 (3 H, t, *J* 6, Me), 1.19–1.53 (8 H, m, 4 × CH₂), 2.15 (2 H, s, CH₂Si) and 2.28 (2 H, t, *J* 7.2, CH₂COCH₂Si); *δ*_C(75 MHz; CDCl₃) –1.15 (q), 13.87 (q), 22.40 (t), 23.96 (t), 28.92 (t), 31.57 (t), 37.95 (t), 44.38 (t) and 209.19 (s, CO); *m/z* 200 (52%, M⁺), 185 (55, M – Me), 143 (89, M – C₄H₉), 115 (100, M – CH₂SiMe₃) and 73 (100, SiMe₃).

1-Cyclohexyl-2-(trimethylsilyl)ethanone **9e**.—In the same way the alcohol **8e** (4 g, 20 mmol) gave the ketone **9e**⁵ (3.75 g, 93%) as a purple oil, b.p. 100–105 °C/0.5 mmHg (lit.⁵ 120 °C/0.5 mmHg); *R*_f 0.70 [ether–light petroleum (1:5, v/v)]; *v*_{max}(film)/cm⁻¹ 1685m (CO) and 850s; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.06 (9 H, s, Me₃Si), 1.10–1.84 (12 H, should be 10 H, m, 5 × CH₂), 2.18 (2 H, s, CH₂Si) and 2.19–2.24 (1 H, m, CH); *δ*_C(75 MHz; CDCl₃) –0.93 (q), 25.77 (t), 25.89 (t), 28.43 (t), 28.57 (t), 28.61 (t), 36.00 (t), 51.99 (d) and 212.49 (s, CO); *m/z* 198 (15%, M⁺), 115 (97, M – C₆H₁₁) and 73 (100, SiMe₃).

1-(Trimethylsilyl)undecan-2-one **9f**.—In the same way the alcohol **8f** (1.35 g, 5.5 mmol) gave the crude ketone **9f** (1.3 g) as an oil; *v*_{max}(film)/cm⁻¹ 2960s, 2860s, 1695s (C=O), 1255s and 860s; *δ*_H(90 MHz; CDCl₃) 0.09 (9 H, s, SiMe₃), 0.85 (3 H, m, Me), 1.25–1.76 (14 H, m, [CH₂]₇), 2.16 (2 H, s, SiCH₂) and 2.30 (2 H, t, *J* 7, COCH₂CH₂) and was used crude in the next reaction.

2-Phenyl-1-(trimethylsilyl)but-3-en-2-ol **10a**.—To a solution of the ketone **9a** (1.9 g, 9.8 mmol) in THF (80 cm³) at 0 °C was added vinylmagnesium bromide (11.3 cm³ of a 1 mol dm⁻³ solution in THF, 11.3 mmol) under nitrogen. The mixture was stirred at 0 °C for 30 min. Standard aq. work-up and chromatography gave the allyl alcohol **10a** (1.69 g, 95%) as an oil, *R*_f 0.42 [ether–light petroleum (1:9, v/v)]; *v*_{max}(film)/cm⁻¹ 3600–3300m (br, OH), 2900s, 2895s, 1490s, 1300s, 920s and 770s; *δ*_H(90 MHz; CDCl₃, pyrazine standard) 0.03 (9 H, s, Me₃Si), 1.29–1.99 (2 H, m, CH₂Si), 2.00 (1 H, s, OH), 5.08–5.57 (2 H, m, CH=CH₂), 6.40 (1 H, dd, *J* 17 and 11, CH=CH₂) and 7.30–7.82 (5 H, m, ArH), which was used crude in the next reaction.

2-Benzyl-1-(trimethylsilyl)but-3-en-2-ol **10b**.—In the same way the ketone **9b** (2 g, 9.7 mmol) and vinylmagnesium bromide (14.5 cm³ of a 1 mol dm⁻³ solution in THF, 14.5 mmol) gave the crude allyl alcohol **10b** (2.02 g) as a yellow oil, *R*_f 0.52 [ether–light petroleum (1:9, v/v)]; *v*_{max}(film)/cm⁻¹ 3500–3300m (br, OH), 1690m (CO, β-keto silane **9b**), 1250s, 845s and 700s; *δ*_H(90 MHz; CDCl₃, pyrazine) 0.13 (s, starting material **9b**) 0.15 (9 H, s, Me₃Si), 1.3 (2 H, s, CH₂Si), 2.3 (s, starting material **9b**), 2.85 (2 H, s, PhCH₂), 3.63 (s, starting material), 4.98–5.27 (2 H, m, CH=CH₂), 6.00 (1 H, dd, *J* 17, 10, CH=CH₂) and 7.1–7.5 (9 H, should be 5 H, m, ArH); OH was not observed. This mixture of starting material **9b** and product **10b** was used without further purification.

5-Phenyl-3-(trimethylsilylmethyl)pent-1-en-3-ol **10c**.—In the same way the ketone **9c** (3 g, 13.63 mmol) and vinylmagnesium bromide (19.08 cm³ of a 1 mol dm⁻³ solution in THF, 19.08 mmol) gave the allyl alcohol **10c** (2.59 g, 78%) as an oil, b.p. 165–167 °C/0.4 mmHg (Found: C, 72.8; H, 9.7. C₁₅H₂₄O_{Si} requires C, 72.51; H, 9.73%); *R*_f 0.57 [ether–light petroleum (4:1, v/v)]; *v*_{max}(film)/cm⁻¹ 3580–3400s (br, OH), 1450s, 1250s, 1030s, 840s and 740; *δ*_H(300 MHz; CDCl₃, pyrazine standard) 0.07 (9 H, s, Me₃Si), 1.11 (2 H, s, CH₂Si), 1.46 (1 H, s, OH), 1.82 (1 H, ddd, *J* 13.6, 9.9 and 6.3, PhCH₂CHaHb), 1.92 (1 H, ddd, *J* 13.6, 9.9 and 6.3, PhCH₂CHaHb), 2.55–2.72 (2 H, m, PhCH₂), 5.11 (1 H, dd, *J* 10.7 and 1.3, CH=CH_{trans}H_{cis}), 5.26 (1 H, dd, *J* 17.29 and 1.30, CH=CH_{trans}H_{cis}), 5.94 (1 H, dd, *J* 17.2 and 10.7, CH=CH₂) and 7.14–7.31 (5 H, m, ArH); *δ*_C(75 MHz; CDCl₃) 0.55 (q), 30.43 (t), 31.54 (t), 45.89 (t), 75.80 (s), 111.41 (t), 128.31 (d), 128.35 (d), 142.50 (s) and 145.58 (d); *m/z* 230 (16, M – H₂O) and 91 (100, PhCH₂); M⁺ peak (*m/z* 248) was not observed.

3-(Trimethylsilylmethyl)non-1-en-3-ol **10d**.—In the same way ketone **9d** (3.2 g, 16 mmol), and vinylmagnesium bromide (20.8 cm³ of a 1 mol dm⁻³ solution in THF, 20.8 mmol) gave a mixture of the allyl alcohol **10d** and starting material **9d** (crude yield 3.42 g) as a yellow oil, *R*_f 0.84 [ether–light petroleum (15:85, v/v)]; *v*_{max}(film)/cm⁻¹ 3600–3400m (br, OH) and 1680m (CO, β-keto silane **9d**); *δ*_H(90 MHz; CDCl₃, pyrazine) 0.12 (9 H, s, Me₃Si), 0.73–2.48 (20 H, should be 16 H, m, 5 × CH₂, SiCH₂, Me and OH), 4.93–5.28 (2 H, m, CH=CH₂) and 5.90 (1 H, dd, *J* 17 and 11, CH=CH₂); this mixture was used in the next stage without further purification.

2-Cyclohexyl-1-(trimethylsilyl)but-3-en-2-ol **10e**.—In the same way the ketone **9e** (3.5 g, 17.6 mmol) and vinylmagnesium bromide (22.9 cm³ of a 1 mol dm⁻³ solution in THF, 22.9 mmol) gave a mixture of the allyl alcohol **10e** and β-keto silane **9e** (crude yield 3.33 g) as a yellow oil, *R*_f 0.60 [ether–light petroleum (1:10, v/v)]; *v*_{max}(film)/cm⁻¹ 3600–3300m (br, CH), 1680m (CO, β-keto silane) and 860s; *δ*_H(90 MHz; CDCl₃, pyrazine) 0.03 (9 H, s, Me₃Si), 0.7–1.94 (13 H, m, 6 × CH₂ and OH), 3.7 (1 H, br s, CH₂CHCH₂), 4.93–5.23 (2 H, m, CH=CH₂) and 5.83 (1 H, dd, *J* 17.5 and 10, CH=CH₂), which was used crude in the next reaction.

3-(Trimethylsilylmethyl)dodec-1-en-3-ol **10f**.—In the same way crude keto silane **9f** (1.3 g, 5.3 mmol) and vinylmagnesium bromide (8 cm³ of a 1 mol dm⁻³ solution in THF, 8 mmol) gave the crude allyl alcohol **10f** (1.06 g) as an oil, $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3480br s, 2960s, 1640w, 1255s, 865s and 845s; $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 0.05 (9 H, s, SiMe₃), 0.84 (3 H, m, Me), 1.02 (2 H, s, SiCH₂), 1.25 (16 H, m, [CH₂]₈), 1.86 (1 H, s, OH), 4.98 (1 H, dd, *J* 10 and 1, CH=CH*cisHtrans*), 5.13 (1 H, dd, *J* 17 and 1, CH=CH*cisHtrans*) and 5.87 (1 H, dd, *J* 17 and 10, CH=CH₂), and was used crude in the next reaction.

2-Phenylbuta-1,3-diene **11a**.—A saturated solution of sodium acetate in glacial acetic acid (6 cm³) was added to the allyl alcohol **10a** (1.6 g, 7.2 mmol) and the mixture was stirred at 60 °C for 30 min before being poured into water (200 cm³) and neutralised to pH 7 (Universal Indicator) with aq. sodium hydrogen carbonate. Standard aq. work-up and flash chromatography gave the diene **11a**²² (0.65 g, 65%) as an oil, b.p. 105–107 °C/10 mmHg (lit.,²² 55–60 °C/15 mmHg); *R*_f 0.74 (light petroleum); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 3080s, 1490m and 775s; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 5.15–5.29 (4 H, m, 2 × CH₂), 6.61 (1 H, dd with further splitting, *J* 17.1 and 11.2, CH=CH₂) and 7.20–7.39 (5 H, m, ArH); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 116.58 (t), 117.02 (t), 127.41 (d), 128.08 (d), 128.20 (d), 138.18 (d), 139.82 (s) and 148.33 (s); *m/z* 130 (100%, M⁺), 103 (11, M – C₂H₃) and 77 (28, Ph).

2-Benzylbuta-1,3-diene **11b**.—In the same way the crude allyl alcohol **10b** (2 g) gave the diene **11b**²³ (0.46 g, 50%) as an oil which decomposed 3 days after preparation, *R*_f 0.67 (light petroleum) (Found: C, 91.3; H, 8.7. Calc. for C₁₁H₁₂: C, 91.6; H, 8.39%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2960s, 1595s, 1450s, 990s and 785s; $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 3.52 (2 H, s, PhCH₂), 4.87 (1 H, br s, C=CH aHb), 5.01 (1 H, d, *J* 10, CH=CH*cisHtrans*), 5.10 (1 H, br s, C=CH aHb), 5.20 (1 H, d, *J* 17, CH=CH*cisHtrans*), 6.37 (1 H, dd, *J* 18 and 11, 3-H) and 7.08–7.36 (5 H, m, ArH); *m/z* 144 (93%, M⁺) and 91 (100, PhCH₂).

2-(2-Phenylethyl)buta-1,3-diene **11c**.—In the same way the allyl alcohol **10c** (1.6 g, 6.4 mmol) gave the diene **11c** (0.72 g, 73%) as an oil, *R*_f 0.63 (light petroleum) (Found: C, 90.9; H, 9.0. C₁₂H₁₄ requires C, 91.08; H, 8.92%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1595s, 900s and 750s; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 2.50 (2 H, t, *J* 9 with further splitting, PhCH₂CH₂), 2.80 (2 H, t, *J* 9 with further splitting, PhCH₂), 4.99 (1 H, br s, CCH aCHb), 5.03 (1 H, br s, CCH aCHb), 5.07 (1 H, d, *J* 11, CH=CH*transHcis*), 5.27 (1 H, d, *J* 18, CH=CH*transHcis*), 6.10 (1 H, dd, *J* 18 and 11, CH=CH) and 7.10–7.35 (5 H, m, ArH); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 33.38 (t), 34.66 (t), 113.16 (t), 115.89 (t), 125.82 (d), 128.28 (d), 128.32 (d), 138.79 (d), 142.76 (s) and 145.76 (s); *m/z* 158 (50%, M⁺) and 91 (100, PhCH₂).

2-Hexylbuta-1,3-diene **11d**.—In the same way the crude allyl alcohol **10d** (3.2 g) gave 2-hexylbuta-1,3-diene **11d**²³ (1.36 g, 70%) as an oil, b.p. 80–83 °C/0.5 mmHg (lit.,²³ 190–200 °C); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2960s, 2920s, 2840s, 1720s, 1595s and 895s; $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 0.83–2.48 (13 H, m, 5 × CH₂ and Me), 4.98 (3 H, br s, CCH₂), and CH=CH*transHcis*), 5.23 (1 H, d, *J* 18, CH=CH*transHcis*) and 6.36 (1 H, dd, *J* 18 and 10, CH=CH₂); *m/z* 138 (9%, M⁺), 109 (10, M – C₂H₅), 81 (21, M – C₄H₉), 68 (100, C₅H₈) and 67 (33, M – C₅H₁₁).

2-Cyclohexylbuta-1,3-diene **11e**.—In the same way the crude allyl alcohol **10e** (3 g) gave 2-cyclohexylbuta-1,3-diene **11e** (1.09 g, 60%) as an oil, b.p. 96–98 °C/0.5 mmHg; *R*_f 0.68 [10% ether–light petroleum (1:9, v/v)]; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1595s, 1580s, 1450s and 895; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 0.85–1.84 (10 H, m, 5 × CH₂), 2.21 (1 H, m, cyclohexyl 1-H), 4.93 (1 H, s with further splitting, CCH aHb), 5.01 (1 H, dd, *J* 10.8 and 1,

CH=CH*transHcis*), 5.26 (1 H, dd, *J* 17.6 and 1, CH=CH*transHcis*) and 6.31 (1 H, dd, *J* 17.6 and 10.8, CH=CH₂); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 26.58 (t), 26.97 (t), 29.73 (t), 32.99 (t), 39.51 (d), 112.29 (t), 112.48 (t), 138.88 (d) and 152.21 (s); *m/z* 136 (52%, M⁺), 121 (100, M – Me), 107 (82, M – C₂H₅), 93 (75, M – C₃H₇) and 53 (33, C₄H₅).

2-Nonylbuta-1,3-diene **11f**.—In the same way the crude allyl alcohol **10f** (1.06 g) gave the diene **11f** (0.59 g, 52% from **7f**) as an oil, *R*_f 0.95 (light petroleum) (Found: C, 86.5; H, 13.4. C₁₃H₂₄ requires C, 86.58; H, 13.42%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 2960s, 2860s, 1640w, 1600m, 905s and 895s; $\delta_{\text{H}}(90 \text{ MHz}; \text{CDCl}_3)$ 0.86 (3 H, t, *J* 6, Me), 1.26 (14 H, m, [CH₂]₇), 2.15 (2 H, t, *J* 8, CH₂CH₂C), 4.92 (2 H, s, CCH₂), 5.01 (1 H, d, *J* 10, CH=CH*cisHtrans*), 5.17 (1 H, d, *J* 18, CH=CH*cisHtrans*) and 6.34 (1 H, dd, *J* 10 and 18, CH=CH₂).

8-Phenyl-3-(2-phenylethyl)-1,6,8-triazabicyclo[4.3.0]non-3-ene-7,9-dione **12c**.—A solution of 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (0.11 g, 0.62 mmol) in dry acetone (1 cm³) was added dropwise to a solution of the diene **11c** (0.09 g, 0.56 mmol) in dry dichloromethane (1 cm³) until a red colour appeared, using the reaction mixture was stirred for 0.5 h at room temperature. Removal of the solvent under reduced pressure and recrystallisation of the residue from methanol gave the triaza dione **12c** (0.14 g, 72%) as crystals, m.p. 136–137 °C (from MeOH) (Found: C, 72.1; H, 5.7; N, 12.6. C₂₀H₁₉N₃O₂ requires C, 72.05; H, 5.74; N, 12.60%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 2850s, 1770s (CO), 1690s (CO) and 735s; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 2.44 (2 H, t, *J* 7.5, PhCH₂CH₂), 2.81 (2 H, t, *J* 7.5, PhCH₂), 4.08 (2 H, br s, C=CCH₂), 4.12 (2 H, br s, C=CCH₂), 5.62 (1 H, br s, CH=C) and 7.16–7.54 (11 H, should be 10 H, m, ArH); $\delta_{\text{C}}(300 \text{ MHz}; \text{CDCl}_3)$ 33.97 (t), 35.92 (t), 43.23 (t), 45.67 (t), 115.41 (d), 125.31, 126.26 (d), 127.94 (d), 128.20 (d), 128.50 (d), 129.03 (d), 131.39 (s), 132.35 (s), 140.57 (s), 152.22 (s) and 152.34 (s); *m/z* 333 (75%, M⁺), 242 (100, M – PhCH₂), 91 (54, PhCH₂) and 77 (6, Ph).

3-Hexyl-8-phenyl-1,6,8-triazabicyclo[4.3.0]non-3-ene-7,9-dione **12d**.—In the same way 2-hexylbuta-1,3-diene **11d** (0.07 g, 0.5 mmol) and 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (0.09 g, 0.51 mmol) gave the triaza dione **12d** (0.12 g, 77%) as a solid, m.p. 119–120 °C (from MeOH) (Found: C, 68.9; H, 7.4; N, 13.4. C₁₈H₂₃N₃O₂ requires C, 68.98; H, 7.36; N, 13.40%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 1780m and 1686m (CO); $\delta_{\text{H}}(400 \text{ MHz}; \text{CDCl}_3)$ 0.88 (3 H, *J* 7, Me), 1.25–1.50 (8 H, m, 4 × CH₂), 2.12 (2 H, t, *J* 7.1, CCH₂CH₂), 4.04 (2 H, s with further splitting, CH₂C=C), 4.13 (2 H, s with further splitting, CH₂C=C), 5.60 (1 H, m, CH=C) and 7.24–7.52 (5 H, m, ArH); $\delta_{\text{C}}(100 \text{ MHz}; \text{CDCl}_3)$ 13.86 (q), 22.37 (t), 27.22 (t), 28.64 (t), 31.40 (t), 34.16 (t), 43.06 (t), 45.41 (t), 114.25 (d), 125.23 (d), 127.84 (d), 128.94 (d), 131.22 (s), 133.04 (s), 152.13 (s) and 152.24 (s); *m/z* 313 (100%, M⁺), 228 (9, M – C₆H₁₃) and 77 (6, Ph).

3-Cyclohexyl-8-phenyl-1,6,8-triazabicyclo[4.3.0]non-3-ene-7,9-dione **12e**.—In the same way 2-cyclohexylbuta-1,3-diene **11e** (0.08 g, 0.5 mmol) and 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (0.12 g, 0.6 mmol) gave the triaza dione **12e** (0.137 g, 76%) as crystals, m.p. 145–146 °C (from MeOH) (Found: C, 69.2; H, 6.8; N, 13.45. C₁₈H₂₁N₃O₂ requires C, 69.42; H, 6.79; N, 13.49%); $\nu_{\max}(\text{Nujol})/\text{cm}^{-1}$ 2870s, 1775m, 1700s (CO) and 770s; $\delta_{\text{H}}(300 \text{ MHz}; \text{CDCl}_3)$ 1.14–2.01 (11 H, m, C₆H₁₁), 4.10–4.15 (4 H, m, CH₂C=CCH₂), 5.62 (1 H, br s, CH=C) and 7.33–7.60 (5 H, m, ArH); $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$ 26.04 (t), 26.39 (t), 31.80 (t), 42.99 (t), 43.33 (d), 44.48 (t), 112.96 (d), 125.34 (d), 127.90 (d), 129.01 (d), 131.46 (s), 138.20 (s), 152.31 (s) and 152.36 (s); *m/z* 311 (10%, M⁺), 228 (27, M – C₆H₁₁), 119 (52, PhNCO), 91 (21, PhN) and 77 (10, Ph).

4-Phenylcyclohex-4-ene-1,2-carboxylic Anhydride 13a.—To a solution of the diene **11a** (0.25 g, 1.9 mmol) in xylene (2 cm³) was added maleic anhydride (0.18 g, 1.9 mmol). After 1 h the crystals were filtered off and washed with light petroleum to give the anhydride **13a** (0.31 g, 70%) as crystals *R*_f 0.33 (light petroleum); m.p. 104 °C (from EtOH) (Found: C, 73.4; H, 5.3. C₁₄H₁₂O₃ requires C, 73.66; H, 5.30%; ν_{\max} (Nujol)/cm⁻¹ 1770s (CO), 1235s, 940s and 825s; δ_{H} (90 MHz; CDCl₃, SiMe₄) 2.16–3.84 (6 H, m, 2 × CH₂ and 2 × CH), 6.01–6.30 (1 H, m, CH=C) and 7.1–7.41 (5 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 24.85 (t), 27.00 (t), 39.68 (d), 40.60 (d), 122.74 (d), 125.44 (d), 127.84 (d), 128.59 (d), 139.72 (s), 140.01 (s) and 173.92 (s); *m/z* 228 (48%, M⁺), 200 (44, M – CO) and 156 (100, M – C₂O₃).

(2RS,3SR)-3-Phenyl-1-(trimethylsilyl)butan-2-ol 15.—By use of the same procedure as for the preparation of compound **8a**, except that the reaction was carried out at –78 °C, 2-phenylpropionaldehyde **14** (2.5 g, 18.6 mmol) and trimethylsilylmethylmagnesium chloride (18.16 cm³ of a 1.3 mol dm⁻³ solution in ether, 24.19 mmol) in ether (200 cm³) gave the silyl alcohol **15** (4 g, 96%) as an oil, b.p. 130–133 °C/0.7 mmHg; *R*_f 0.40 (10% ether–light petroleum) (Found: C, 70.1; H, 9.8. C₁₃H₂₂O_{Si} requires C, 70.20; H, 9.97%; ν_{\max} (film)/cm⁻¹ 3500–3200m (br, OH), 2960s, 1250s and 860s; δ_{H} (300 MHz; CDCl₃, pyrazine) 0.04 (9 H, s, Me₃Si), 0.71 (1 H, s with further splitting, SiCHaHb), 0.75 (1 H, s, SiCHaHb), 1.32 (3 H, d, *J* 7, Me), 2.76–2.80 (1 H, m, PhCH), 3.86–3.93 (1 H, m, CHOH) and 7.20–7.36 (6 H, should be 5 H, m, ArH); OH was not observed; δ_{C} (75 MHz; CDCl₃) 0.05 (q, Me₃Si), 15.67 (q), 23.97 (t), 48.98 (d), 75.04 (d), 127.13 (d), 128.66 (d), 129.20 (d) and 145.49 (s); *m/z* 222 (0.1%, M⁺) 204 (12, M – H₂O), 189 (5, M – Me – H₂O) and 73 (100, SiMe₃).

3-Phenyl-1-(trimethylsilyl)butan-2-one 16.—By use of the same procedure as for the preparation of compound **9a**, silyl alcohol **15** (3.8 g, 17.1 mmol) and a preformed solution of chromium(vi) oxide (11.34 g, 114.6 mmol) and pyridine (11.93 g, 142.2 mmol) in dichloromethane (300 cm³) gave the silyl ketone **16** (3.35 g, 89%) as an oil, b.p. 100–103 °C/0.7 mmHg; *R*_f 0.66 [ether–light petroleum (1:4, v/v)]; ν_{\max} (film)/cm⁻¹ 3080m, 3060m, 3020m, 2960s, 2900m, 2870m, 1685s (CO), 1450s, 1250s, 1110s, 1030s, 850s and 750s; δ_{H} (300 MHz; CDCl₃, pyrazine) 0.07 (9 H, s, Me₃Si), 1.36 (3 H, d, *J* 7, Me), 2.03 (1 H, d with further splitting, *J* 10, SiCHaCHb), 2.30 (1 H, d, *J* 10, SiCHaCHb), 3.66 (1 H, q, *J* 7, PhCH) and 7.19–7.38 (5 H, m, Ph); δ_{C} (75 MHz; CDCl₃) –1.04 (q), 17.73 (q), 36.60 (t), 54.08 (d), 126.90 (d), 127.73 (d), 127.88 (d), 140.87 (s) and 209.03 (s); *m/z* 220 (62%, M⁺), 205 (51, M – Me), 115 (62, OCCH₂SiMe₃) and 73 (100, SiMe₃).

(1RS)-1-[(1SR)-1-Phenylethyl]-1-(trimethylsilylmethyl)prop-2-enol 17.—Following the same procedure as for the preparation of compound **10a**, except that the reaction was carried out at –78 °C, ketone **16** (3.5 g, 15.9 mmol), and vinylmagnesium bromide (20.6 cm³ of a 1 mol dm⁻³ solution in THF) in THF (100 cm³) gave the allyl alcohol **17** (1.53 g, 38%) as an oil, b.p. 120–122 °C/1 mmHg; *R*_f 0.73 [ether–light petroleum (1:9, v/v)]; ν_{\max} (film)/cm⁻¹ 3600–3300m (br, OH), 1600m, 1250s and 850s; δ_{H} (300 MHz; CDCl₃, pyrazine) 0.01 (9 H, s, Me₃Si), 0.94 (1 H, d, *J* 14.7, SiCHaCHb), 1.03 (1 H, d, with further splitting, *J* 14.7, SiCHaCHb), 1.28 (3 H, d, *J* 7.2, Me), 1.59 (1 H, s, with further splitting, OH), 3.81 (1 H, q, *J* 7.2, PhCH), 5.09 (1 H, dd, *J* 17.60 and 1.4, CH=CH_{trans}H_{cis}), 5.12 (1 H, dd, *J* 10.30 and 1.4, CH=CH_{trans}H_{cis}), 5.89 (1 H, dd, *J* 17.60 and 10.3, CH=CH₂) and 7.19–7.33 (5 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 0.61 (q), 16.38 (q), 28.84 (t), 52.00 (d), 77.66 (s), 112.48 (t), 126.54 (d), 127.83 (d), 129.37 (d), 142.42 (s) and 143.48

(d); *m/z* 230 (92, M – H₂O), 215 (24, M – H₂O – Me) and 73 (100, SiMe₃).

2-(1-Phenylethyl)buta-1,3-diene 18.—Following the same procedure as for the preparation of compound **11a**, allyl alcohol **17** (1.3 g, 5.2 mmol) and a saturated solution of sodium acetate in glacial acetic acid (2 cm³) gave the diene **18** (0.606 g, 73%) as an oil, b.p. 90 °C/0.5 mmHg; *R*_f 0.73 (light petroleum); ν_{\max} (film)/cm⁻¹ 2970s, 2890m, 1595m, 1490m and 900s; δ_{H} (300 MHz; CDCl₃) 1.40 (3 H, d, *J* 7, Me), 3.77 (1 H, q, *J* 7, PhCH), 4.95 (1 H, d with further splitting, *J* 10.9, CH=CH_{cis}H_{trans}), 5.14 (2 H, s with further splitting, CCH₂), 5.20 (1 H, d with further splitting, *J* 17.6, CH=CH_{cis}H_{trans}), 6.30 (1 H, dd, *J* 17.60 and 10.9, CH=CH₂) and 7.13–7.29 (5 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 21.64 (q), 40.96 (d), 114.31 (t), 115.30 (t), 126.04 (d), 127.29 (d), 128.38 (d), 138.49 (d), 145.56 (s) and 149.68 (s); *m/z* 158 (100%, M⁺), 143 (98, M – Me), 129 (81, M – C₂H₅) and 77 (40, Ph).

8-Phenyl-3-(1-phenylethyl)-1,6,8-triazabicyclo[4.3.0]non-3-ene-7,9-dione 19.—Following the same procedure as for the preparation of compound **12c**, reaction of diene **18** (0.85 g, 0.5 mmol) in dichloromethane (1 cm³) with 4-phenyl-1,2,4-triazole-3,5(4H)-dione (0.098 g, 6 mmol) in acetone (1 cm³) gave the triaza dione **19** (0.165 g, 92%) as a thick oil, ν_{\max} (film)/cm⁻¹ 1770s, 1710s (CO), 1600m, 1400s, 1295s, 1145s and 790s; δ_{H} (300 MHz; CDCl₃) 1.51 (3 H, d, *J* 7, Me), 3.56 (1 H, q, *J* 7, PhCH), 3.92–3.94 (2 H, m, CH₂), 4.22–4.25 (2 H, m, CH₂), 5.88–5.90 (1 H, m, C=CH) and 7.25–7.52 (12 H, should be 10 H, m, ArH); δ_{C} (75 MHz; CDCl₃) 15.05 (q), 43.18 (t), 43.69 (d), 44.75 (t), 114.19 (d), 125.32 (d), 125.39 (d), 126.87 (d), 127.12 (d), 127.99 (d), 128.69 (d), 129.01 (d), 131.01 (s), 136.63 (s), 152.10 (s) and 152.24 (s); *m/z* 333 (100%, M⁺), 228 (18, M – C₂H₅), 119 (25, PhNCO), 91 (14, PhN) and 77 (12, Ph) (Found: M⁺, 333.1472. C₂₀H₁₉N₃O₂ requires M, 333.1477).

(2S,2'S)-2'-(Benzyloxymethoxy)propyl 3,3,3-Trifluoro-2-methoxy-2-phenylpropionate 23.—To a solution of (2S)-2-(benzyloxymethoxy)propan-1-ol¹³ **21** (0.1 g, 0.5 mmol) in dichloromethane (2 cm³) were added 1,3-dicyclohexylcarbodiimide (DCC) (0.157 g, 0.7 mmol), 3,3,3-trifluoro-2-methoxy-2-phenylpropionic acid (0.179 g, 0.7 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.062 g, 0.5 mmol) in dichloromethane (3 cm³) under nitrogen. The reaction mixture was stirred for 4 h at room temperature, after which a solid formed. After removal of the solvent under reduced pressure, light petroleum (10 cm³) was added to the well stirred residue. The solid was filtered off and the filtrate was washed successively with dil. hydrochloric acid (3 × 5 cm³) and water (3 × 10 cm³) and then dried (MgSO₄). Flash chromatography gave the ester **23** (0.156 g, 74%) as an oil, b.p. 185–188 °C/0.7 mmHg; *R*_f 0.7 (20% ether–light petroleum) (Found: C, 61.2; H, 5.7. C₂₁H₂₃F₃O₅ requires C, 61.15; H, 5.62%; ν_{\max} (film)/cm⁻¹ 1750s (CO, ester), 1280s, 1170s and 1040s; δ_{H} (300 MHz; CDCl₃) 1.21 (3 H, d, *J* 6.5, CHMe), 3.55 (3 H, s with further splitting, OMe), 3.98–4.08 (1 H, m, MeCH), 4.27 (1 H, dd, *J* 11.4 and 6.5, CHCHaHbO), 4.32 (1 H, dd, *J* 11.4 and 6.5, CHCHaHbO), 4.52 (1 H, d, *J* 11.8, PhCHaHb), 4.58 (1 H, d, *J* 11.8, PhCHaHb), 4.72 (1 H, d, *J* 7.1, OCHaHbO), 4.76 (1 H, d, *J* 7.1, OCHaHbO) and 7.25–7.54 (10 H, m, ArH); δ_{F} (100 MHz; CDCl₃) 65.32 (s) (crude).

(2R,3S)-3-(Benzyloxymethoxy)-1-(trimethylsilyl)butan-2-ol 24.—Following the same procedure as for the preparation of compound **8a**, except that the reaction was carried out at –78 °C, (2S)-2-(benzyloxymethoxy)propanal¹³ **22** (0.5 g, 2.5 mmol) and trimethylsilylmagnesium chloride (2.5 cm³ of a 1.3 mol dm⁻³ solution in ether, 3.27 mmol) in ether (50 cm³) gave

the silyl alcohol **24** (0.65 g, 89%) as an oil, b.p. 140–143 °C/0.8 mmHg; R_f 0.57 [ether–light petroleum (1:4, v/v)]; $[\alpha]_D^{20}$ –27.44° (*c* 0.84 in EtOH) (Found: C, 63.7; H, 9.2. $C_{15}H_{26}O_3Si$ requires C, 63.78; H, 9.27%); ν_{max} (film)/ cm^{-1} 3600–2900m (br, OH), 1250s, 1150s, 1030s, 860s and 700s; δ_H (300 MHz; $CDCl_3$, pyrazine) 0.07 (9 H, s, Me_3Si), 0.72 (1 H, s, $CHaHbSi$), 0.75 (1 H, s, with further splitting, $CHaHbSi$), 1.19 (3 H, d, *J* 6.1, *MeCH*), 1.63 (1 H, s, OH), 3.50 (1 H, quint, *J* 6.1, *MeCH*), 3.56–3.64 (1 H, m, *CHOH*), 4.65 (2 H, s, with further splitting, $PhCH_2$), 4.82 (1 H, d, *J* 6.7, *OCHaHbO*), 4.87 (1 H, b of AB system, d, *J* 6.7, *OCHaHbO*) and 7.27–7.47 (5 H, m, ArH); δ_C (75 MHz; $CDCl_3$) –0.67 (q), 16.83 (q), 21.0 (t), 69.71 (t), 73.19 (d), 80.74 (d), 93.99 (t), 127.70 (d), 127.80 (d), 128.38 (d) and 137.56 (s); *m/z* 145 (16, M – $PhCH_2OCH_2O$), 117 (70, $HOCHCH_2SiMe_3$) and 73 (100, $SiMe_3$).

(3S)-3-(Benzyloxymethoxy)-1-(trimethylsilyl)butan-2-one

25.—Following the same procedure as for the preparation of compound **9a**, the silyl alcohol **24** (3.4 g, 12 mmol) and a preformed solution of chromium(vi) oxide (7.99 g, 80 mmol) and pyridine (8.40 g, 100 mmol) in dichloromethane (300 cm^3) gave a mixture of silyl ketone **25** and silyl alcohol **24** (3.26 g) as a yellow oil, R_f 0.44 [ether–light petroleum (1:4, v/v)]; ν_{max} (film)/ cm^{-1} 3600–3300br (OH), 2950s, 2890s, 1690s (CO), 1250s, 1170s, 1120–980s (br), 850s and 740s; δ_H (90 MHz; $CDCl_3$, pyrazine) 0.15 (9 H, s, Me_3Si), 1.34 (3 H, d, *J* 6.5, *MeCH*), 2.16–2.50 (2 H, m, CH_2Si), 4.13 (1 H, q, *J* 6.5, *MeCH*), 4.60–5.00 (4 H, m, $PhCH_2OCH_2$) and 7.31 (5 H, br s, ArH), and was used crude in the next reaction.

(3S,4S)- and (3R,4S)-4-(Benzyloxymethoxy)-3-(trimethylsilylmethyl)pent-1-en-3-ol **26a/b**.—Following the same procedure as for the preparation of compound **10a**, except that the reaction was carried out at –78 °C, crude silyl ketone **25** (3 g), from the previous preparation, and vinylmagnesium bromide (13.9 cm^3 , 13.9 mmol, 1 mol dm^{-3} solution in THF) in THF (100 cm^3) gave the silyl alcohols **26a/b** (0.706 g, 20% from **24**) as an oil, which was a 2:1 mixture of diastereoisomers, b.p. 130–134 °C/0.7 mmHg; R_f 0.31 [ether–light petroleum (1:9, v/v)]; ν_{max} (film)/ cm^{-1} 3680–3450m (br, OH), 1250s, 1040s, 860s and 700s; δ_H (400 MHz; $CDCl_3$, pyrazine) diastereoisomer **26a**: 0.04 (9 H, s, Me_3Si), 1.18 (3 H, d, *J* 3.7, *MeCH*), 3.53 (1 H, q, *J* 7, *MeCH*), 5.13 (1 H, dd, *J* 10.7 and 1.6, $CH=CH_{cis}H_{trans}$), 5.30 (1 H, dd, *J* 17.2 and 1.6, $CH=CH_{cis}H_{trans}$) and 5.84 (1 H, dd, *J* 17.2 and 10.7, $CH=CH_2$); Diastereoisomer **26b**: 0.057 (9 H, s, Me_3Si), 1.20 (3 H, d, *J* 7, *MeCH*), 3.60 (1 H, q, *J* 7, *MeCH*), 5.17 (1 H, dd, *J* 10.7 and 1.6, $CH=CH_{cis}H_{trans}$), 5.35 (1 H, dd, *J* 17.2 and 1.6, $CH=CH_{cis}H_{trans}$) and 5.93 (1 H, dd, *J* 17.2 and 10.7, $CH=CH_2$); common peaks for both diastereoisomers **26a** and **26b**: 0.89–1.11 (2 H, m, $SiCH_2$), 1.63 (1 H, br s, OH), 4.62 (1 H, d, *J* 12, $PhCHaHb$), 4.67 (1 H, d, *J* 12, $PhCHaHb$), 4.78–4.90 (2 H, m, OCH_2O) and 7.24–7.38 (5 H, m, ArH); δ_C (100 MHz; $CDCl_3$) 0.47 and 0.53 (2 q), 15.01 and 15.37 (2 q), 24.04 and 26.36 (2 t), 69.69 and 69.83 (2 t), 77.21 and 77.34 (2 s), 81.82 and 82.71 (2 d), 94.09 and 94.32 (2 t), 113.27 and 113.36 (2 t), 127.58 (d), 127.61 (d), 127.64 (d), 127.66 (d), 128.30 (d), 137.56 (s), 141.50 (d) and 143.14 (d); $[\alpha]_D^{20}$ +21.81° (*c* 0.48 in CH_2Cl_2); *m/z* 91 (100, $PhCH_2$) and 77 (11, Ph).

(1'S)-2-[1'-(Benzyloxymethoxy)ethyl]buta-1,3-diene **27**.—

Following the same procedure as for the preparation of compound **11a**, the alcohols **26a/b** (0.5 g, 1.6 mmol) and a saturated solution of sodium acetate in glacial acetic acid (2 cm^3) gave the diene **27** (0.35 g, 71%) as an oil, R_f 0.75 [ether–light petroleum (1:9, v/v)] (Found: C, 76.7; H, 8.4. $C_{14}H_{18}O_2$ requires C, 77.02; H, 8.31%); $[\alpha]_D^{20}$ –115.05° (*c* 0.25 in CH_2Cl_2); ν_{max} (film)/ cm^{-1} 3080m, 3030m, 2980s, 2880s, 1590m, 1500m, 1450m, 1370m, 1260w, 1180m, 1105s, 1040s and 1025;

δ_H (400 MHz; $CDCl_3$, pyrazine) 1.37 (3 H, d, *J* 6.5, *MeCH*), 4.53–4.59 (2 H, m, $PhCH_2$), 4.68–4.76 (3 H, m, OCH_2O and *MeCH*), 5.11 (1 H, d, *J* 11 $CH=CH_{cis}H_{trans}$), 5.18 (1 H, s, $C=CHaHb$), 5.22 (1 H, s, $C=CHaHb$), 5.38 (1 H, d with further splitting, *J* 17, $CH=CH_{cis}H_{trans}$), 6.34 (1 H, dd with further splitting, *J* 17 and 11, $CH=CH_2$) and 7.25–7.37 (5 H, m, ArH); δ_C (100 MHz; $CDCl_3$) 21.30 (q), 69.46 (t), 72.08 (d), 92.21 (t), 114.50 (t), 114.62 (t), 127.50 (d), 127.76 (d), 128.27 (d), 135.77 (d), 137.98 (s) and 147.42 (s); *m/z* 91 (90, $PhCH_2$) and 77 (19, Ph).

(1'S)-3-[1'-(Benzyloxymethoxy)ethyl]-8-phenyl-1,6,8-triazabicyclo[4.3.0]non-3-ene-7,9-dione **28**.—Following the same procedure as for the preparation of compound **12c**, reaction of the diene **27** (0.09 g, 0.4 mmol) in dichloromethane (1 cm^3) with 4-phenyl-1,2,4-triazole-3,5(4*H*)-dione (0.089 g, 0.5 mmol) in acetone (1 cm^3) gave the triaza dione **28** (0.153 g, 94%) as a thick oil; ν_{max} (film)/ cm^{-1} 1770s, 1700s (CO), 1490s, 1290s, 1135s, 800s and 700s; δ_H (400 MHz; $CDCl_3$) 1.38 (3 H, d, *J* 6.6, *MeCH*), 4.14–4.21 (4 H, m, 2 × CH_2), 4.45 (1 H, q, *J* 6.6, *MeCH*), 4.59 (1 H, d, *J* 11.7, $PhCHaHb$), 4.70 (1 H, d, *J* 11.7, $PhCHaHb$), 4.76–4.85 (2 H, br s, OCH_2O), 5.92–5.94 (1 H, m, $C=CH$) and 7.31–7.54 (10 H, m, ArH); *m/z* 393 (M^+ , 3%), 137 (6, $PhCH_2OCH_2O$), 121 (6, $PhCH_2OCH_2$), 107 (7, $PhCH_2O$), 91 (100, $PhCH_2$) and 77 (19, Ph) (Found: M^+ , 393.1665. $C_{22}H_{23}N_3O_4$ requires M , 393.1688).

(1'S,1R,2S) and (1'S,1S,2R)-4-[1'-(Benzyloxymethoxy)ethyl]-N-phenyl-cyclohex-4-ene-1,2-dicarboximide **29a/b**.—

N-Phenylmaleimide (0.039 g, 0.2 mmol) was added to a mixture of the diene **27** (0.05 g, 0.2 mmol) in dry toluene (3 cm^3) under nitrogen. The reaction mixture was heated under reflux for 4 h. Removal of the solvent under reduced pressure, and purification on preparative silica gel plates, gave the imides **29a/b** (0.050 g, 56%) as an oily 1:1.28 mixture of diastereoisomers, R_f 0.18 [ether–light petroleum (1:1, v/v)]; ν_{max} (film)/ cm^{-1} 1710s (CO); δ_H (300 MHz; $CDCl_3$) 1.20 (3 H, d, *J* 6.5, *MeCH*, **27a**), 1.22 (3 H, d, *J* 6.5, *MeCH*, **27b**), 2.23–2.33 (2 H, m, CH_2), 2.69–2.80 (2 H, m, CH_2), 3.19–3.32 (2 H, m, 2 × CH), 4.24 (1 H, quint, *J* 6.5, *CHMe*), 4.45–4.69 (4 H, m, $PhCH_2OCH_2$), 5.86–5.89 (1 H, m, $C=CH$) and 7.18–7.48 (11 H, should be 10 H, m, ArH); δ_C (75 MHz; $CDCl_3$) 10.72 (q), 23.49 and 23.63 (2 t), 23.93 (t), 69.44 (t), 73.85 (d), 74.71 (d), 91.78 and 91.91 (2 t), 122.42 (d), 123.21 (d), 126.16 (d), 126.20 (d), 127.58 (d), 127.74 (d), 128.32 (d), 128.45 (d), 129.02 (d), 130.11 (s), 140.86 (s), and 178.61 and 178.88 (2 s).

(1'S,1R,2R) and (1'S,1S,2S)-4-[1'-(Benzyloxymethoxy)ethyl]-cyclohex-4-ene-1,2-dicarboxylate **30a/b**.—

Following the same procedure as for the preparation of compounds **29a/b** the diene **27** (0.05 g, 0.2 mmol) and diethyl fumarate (0.039 g, 0.2 mmol) in toluene (3 cm^3) gave the diesters **30a/b** (0.055 g, 61%) as an oily 1:1.3 mixture of diastereoisomers, R_f 0.48 [ether–light petroleum (3:7, v/v)]; ν_{max} (film)/ cm^{-1} 1730s (CO), 1440s, 1180s, 1100s and 735s; δ_H (300 MHz; $CDCl_3$) 1.21–1.37 (9 H, m, 3 × Me), 2.08–2.87 (6 H, m, 2 × CH_2 , and 2 × CH), 4.10–4.26 (4 H, m, 2 × OCH_2Me), 4.51–4.68 (5 H, m, $PhCH_2OCH_2OCH$), 5.66 (1 H, br s, $C=CH$) and 7.26–7.35 (5 H, m, ArH); δ_C (75 MHz; $CDCl_3$) 14.11, 19.41, 19.82, 25.79, 25.92, 27.45, 27.77, 41.22, 41.30, 41.44, 41.48, 60.52, 60.57, 69.44, 75.01, 75.11, 91.58, 91.70, 121.60, 122.44, 127.56, 127.70, 128.30, 136.35, 137.89, 174.51 and 174.66.

Acknowledgements

We acknowledge the financial support of the SERC (P. A. B., R. V. B.), Pharmachemie BV of Holland (N. J. L.), and the Egyptian Government (M. R. S.).

References

- 1 P. A. Brown, R. V. Bonnert, P. R. Jenkins and M. R. Selim, *Tetrahedron Lett.*, 1987, **28**, 693.
- 2 M. J. Carter and I. Fleming, *J. Chem. Soc., Chem. Commun.*, 1976, 679.
- 3 I. Fleming, M. J. Carter and A. Percival, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2415.
- 4 T. H. Chan, E. Chang and E. Vinoker, *Tetrahedron Lett.*, 1970, 1137; D. J. Morgans and G. Stork, *Tetrahedron Lett.*, 1979, 1959; T. Hirao, A. Yamada, K.-I. Hayashi, Y. Oshiro and T. Agawa, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1163; R. T. Taylor and J. G. Galloway, *J. Organomet. Chem.*, 1981, **220**, 295; C.-N. Hsiao and H. Schecter, *Tetrahedron Lett.*, 1984, **25**, 1219; J.-P. Pillot, J. Dunogues and R. Calas, *J. Chem. Res. (S)*, 1977, 268; D. M. Hollinshead, S. C. Howel, S. V. Ley, M. Mahon, N. M. Ratcliffe and P. M. Worthington, *J. Chem. Soc., Chem. Commun.*, 1983, 1579; S. Halazy, W. Dumont and A. Krief, *Tetrahedron Lett.*, 1981, **22**, 4737; T. Cohen, J. P. Sherbine, J. R. Matz, R. R. Huthings, B. M. McHenry and P. R. Willey, *J. Am. Chem. Soc.*, 1984, **106**, 3245; P. W. K. Lau and T. H. Chan, *Tetrahedron Lett.*, 1978, 2383; E. Ehlinger and P. Magnus, *J. Am. Chem. Soc.*, 1980, **102**, 5004; R. Corriu and J. Masse, *J. Organomet. Chem.*, 1973, **57**, C5; F. Sato, Y. Suzuki and M. Sato, *Tetrahedron Lett.*, 1982, **23**, 4589; F. Sato, H. Uchiyama, K. Iida, Y. Kobayashi and M. Sato, *J. Chem. Soc., Chem. Commun.*, 1983, 921; T. H. Chan and J.-S. Li, *J. Chem. Soc., Chem. Commun.*, 1982, 969; D. J. S. Tsai and D. S. Mateson, *Tetrahedron Lett.*, 1981, **22**, 2751. For examples of vinylogous Peterson elimination see A. G. Angoh and D. L. J. Clive, *J. Chem. Soc., Chem. Commun.*, 1984, 534; I. Fleming, I. T. Morgan and A. K. Sarkar, *J. Chem. Soc., Chem. Commun.*, 1990, 1575.
- 5 R. A. Ruden and B. L. Gaffney, *Synth. Commun.*, 1975, **5**, 15.
- 6 Y. Yamamoto, K. Ohdoi, M. Nakatani and K. Akiba, *Chem. Lett.*, 1984, 1967.
- 7 K. Oertle, H. Beyeler, R. O. Duthaler, W. Lottenbach, M. Riediker and E. Steiner, *Helv. Chim. Acta*, 1990, **73**, 353.
- 8 D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780; D. J. Ager, *Org. React.*, 1990, **38**, 1.
- 9 R. C. Cookson, S. S. H. Gilani and I. D. R. Stevens, *J. Chem. Soc. C*, 1967, 1905.
- 10 (a) D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, 1952, **74**, 5828; (b) K. R. Kopecky and D. J. Cram, *J. Am. Chem. Soc.*, 1959, **81**, 2748; (c) T. J. Leitereg and D. J. Cram, *J. Am. Chem. Soc.*, 1968, **90**, 4019; (d) M. Cherest, H. Felkin and N. Prudent, *Tetrahedron Lett.*, 1968, 2199; (e) N. T. Anh and O. Eisenstein, *Nouv. J. Chim.*, 1977, **1**, 61.
- 11 (a) M. T. Reetz, S. H. Kyuang and M. Hillmann, *Tetrahedron*, 1986, **42**, 2931; (b) Y.-D. Wu and K. N. Houk, *J. Am. Chem. Soc.*, 1987, **109**, 908; (c) B. H. Lipshutz, E. L. Ellsworth and T. J. Siahhan, *J. Am. Chem. Soc.*, 1988, **110**, 4834; (d) O. Arjona, R. Perez-Ossorio, A. Perez-Rubalcaba and M. L. Quiroja, *J. Chem. Soc., Perkin Trans. 2*, 1981, 597; (e) Y. Yamamoto and K. Maruyama, *J. Am. Chem. Soc.*, 1985, **107**, 6411; (f) P. R. Jones, E. J. Goller and W. J. Kauffman, *J. Org. Chem.*, 1971, **36**, 3311; (g) Y. Kodoma, K. Nishihata, S. Zushi, M. Nishio, J. Uzawa, K. Sakamoto and H. Iwamura, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 2661.
- 12 C. Alvarez-Ibarra, O. Arjona, R. Perez-Ossorio, A. Perez-Rubalcaba, M. L. Quiroja and M. J. Santemases, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1645.
- 13 (a) G. Stork and A. F. Kreft, *J. Am. Chem. Soc.*, 1977, **99**, 3851; (b) L. Banfi, A. Bernardi, L. Colombo, C. Genarri and C. Scolasti, *J. Org. Chem.*, 1984, **49**, 3784.
- 14 S. D. Burke, F. J. Schoenen and C. W. Murtiashaw, *Tetrahedron Lett.*, 1986, **27**, 449.
- 15 V. J. Jephcote, A. J. Pratt and E. J. Thomas, *J. Chem. Soc., Chem. Commun.*, 1984, 800.
- 16 P. R. Jenkins and D. A. Dawkins, unpublished work.
- 17 B. M. Trost, D. O'Krongly and J. L. Belletire, *J. Am. Chem. Soc.*, 1980, **102**, 7595; R. C. Gupta, P. A. Harland and R. J. Stoodley, *J. Chem. Soc., Chem. Commun.*, 1983, 754; *Tetrahedron*, 1984, **40**, 4657; R. C. Gupta, C. M. Raynor, R. J. Stoodley, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1773; W. G. Dauben and R. A. Bunce, *Tetrahedron Lett.*, 1982, **23**, 4875; R. W. Frank, S. Argade, C. S. Subramaniam and D. M. Frechet, *Tetrahedron Lett.*, 1982, **23**, 3187; R. Tripathy, R. W. Frank and K. D. Onan, *J. Am. Chem. Soc.*, 1988, **110**, 3257; A. Lubineau and Y. Queneau, *Tetrahedron Lett.*, 1985, **26**, 2653; *J. Org. Chem.*, 1987, **52**, 1001; P. G. McDougal, J. M. Jump, C. Rojas and J. G. Rico, *Tetrahedron Lett.*, 1989, **30**, 3897; A. P. Kozikowski, T. R. Nieduzak, T. Konoike and J. P. Springer, *J. Am. Chem. Soc.*, 1987, **109**, 5167; M. J. Fisher, W. J. Hehre, S. D. Khan and L. E. Overman, *J. Am. Chem. Soc.*, 1988, **110**, 4625; C. W. Bird and A. Lewis, *Tetrahedron Lett.*, 1989, **30**, 6227.
- 18 W. C. Still, M. Khan and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2943.
- 19 F. A. Carey and J. R. Toler, *J. Org. Chem.*, 1976, **41**, 1966.
- 20 P. Sampson, G. B. Hammond and D. F. Wiemer, *J. Org. Chem.*, 1986, **51**, 4342.
- 21 T. Benneche, M. L. Christiansen and K. Undheim, *Acta Chem., Scand., Ser. B*, 1986, **40**, 700.
- 22 C. C. Price, F. L. Benton and C. J. Schmidle, *J. Am. Chem. Soc.*, 1949, **71**, 2860.
- 23 Y. Ueno, H. Sano, S. Aoki and M. Okawara, *Tetrahedron Lett.*, 1981, **22**, 2675.

Paper 1/01027A

Received 5th March 1991

Accepted 15th April 1991