The Synthesis of *E* Enol Ethers of Protected 4-Amino Aldehydes

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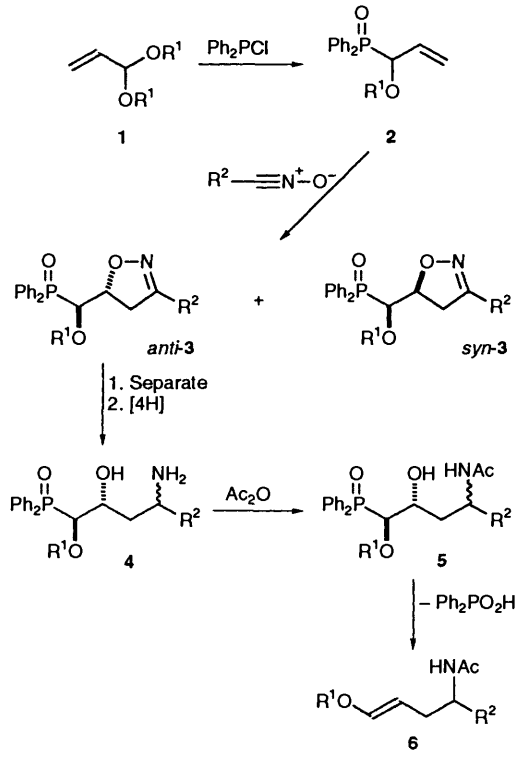
The title compounds, a novel class of protected homoallylic amines, have been synthesised by a short and efficient route. Acrolein acetals were converted by a modified Michaelis–Arbuzov reaction into α-alkoxyallyl(diphenyl)phosphine oxides. 1,3-Dipolar cycloaddition to the alkene part of these molecules gave 5-diphenylphosphinoyl-4,5-dihydroisoxazoles, which were reductively cleaved to obtain δ-amino-β-hydroxy-α-alkoxyalkyl(diphenyl)phosphine oxides. After selective protection as the *N*-acetyl derivatives, stereospecific Wittig–Horner diphenylphosphinic acid elimination gave the title compounds.

The title compounds **6** are a functionalised and protected class of homoallylic primary amines **7** which, to our knowledge, have not been synthesised before. In this paper, we present an efficient five-step synthesis of these novel compounds, as outlined in Scheme 1. In our synthesis, the carbon–carbon double bond



Scheme 1

in the enol ethers **6** was created by a Horner–Wittig elimination. The necessary β-hydroxyalkylphosphine oxide derivatives **4** were set up in a latent form by nitrile oxide cycloaddition to α-alkoxyallyl(diphenyl)phosphine oxides **2**. Reductive ring cleavage of the resulting isoxazolines *anti*-**3** then unmasked the hydroxy group, as well as giving rise to the primary amino group in **4**. Protection of this function as an amide (in **5**) was necessary before completing the synthesis by stereospecific elimination of diphenylphosphinic acid to give the product enol ethers **6**.

Allylic acetals **1** were converted by the Michaelis–Arbuzov strategy of Miller and co-workers[1] into α-alkoxyallyl(diphenyl)phosphine oxides **2**. The reaction worked well with acrolein diethyl acetal **1b**, as well as the dimethyl acetal of the original report, but contrary to that report we found these phosphine oxides difficult to recrystallise and unstable to heat. We therefore did not purify them before use.

Table 1 Cycloadditions of alkenes **2** and nitrile oxides

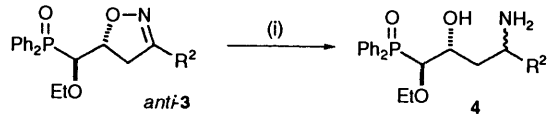
Alkene **2**	R^1	Isoxazole **3**	R^2	Yield (%) (*anti*-**3** + *syn*-**3**)	Ratio *anti*-**3**:*syn*-**3**
a	Me	**a**	Pr	27[a]	70:30
a	Me	**b**	Ph	66[b]	76:24
b	Et	**c**	Pr	63	67:33
b	Et	**d**	Ph	63	80:20

[a] Yield of *anti*-**3** after fractional crystallisation. [b] Sonication of the reaction mixture gave the same diastereoisomeric ratio in 52% yield.

Nitrile oxide cycloadditions to alkenes **2** were straightforward, if slow (typically requiring 5 days for completion), under our standard conditions.[2] These were heterogeneous, involving aqueous NaOCl (bleach) above a dichloromethane solution of the alkene and an aldehyde oxime as the nitrile oxide precursor. Nitrile oxide cycloaddition to unfunctionalised allylphosphine oxides[2] is accelerated by ultrasound, as are other [1,3]-dipolar cycloadditions.[3] However, these cycloadditions of α-alkoxyallyl(diphenyl)phosphine oxides **2** were not appreciably accelerated by sonication.

As expected with a monosubstituted electron-rich double bond, the cycloadditions were totally regioselective, giving only the 3,5-disubstituted adducts **3**. The reactions were also moderately stereoselective, giving mixtures of *anti*-**3** and *syn*-**3** in which the *anti* compounds always predominated (see Table 1). This is consistent with the transition state model of Houk and co-workers.[4] However, the reactions were *less* stereoselective than those of the corresponding α-alkyl substituted phosphine oxides **8**.[2] The Houk model predicts the opposite, and it has been generally observed that allylic ethers are *more* stereoselective than similar α-alkyl alkenes.[4,5] The unusually poor selectivity of our alkenes is not understood.

The two diastereoisomeric cycloadducts *anti*-**3** and *syn*-**3** had very similar R_F values, and could not be separated by flash column chromatography, unlike the analogous non-oxygenated compounds *anti*- and *syn*-**9**.[2] The major isomers, *anti*-**3**, could be isolated by fractional crystallisation, but the minor isomers, *syn*-**3**, were never isolated. The stereochemistry was confirmed both by NMR correlations to compound *anti*-**10**, of which an X-ray crystal structure had been obtained,[2,6] and by chemical conversion (see below).

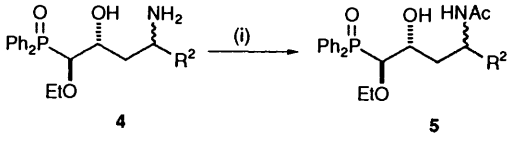


(i) $NaBH_4$, $NiCl_2.6H_2O$, MeOH, –30 °C
3a, 4a: R^2 = Pr, 98%, 50:50
3b, 4b: R^2 = Ph, 97%, 71:29

Scheme 2

The isoxazolines *anti*-**3** were reduced cleanly and in high yield to the corresponding amino alcohols **4** using sodium borohydride and nickel(II) chloride hexahydrate.[2,7] The reductions proceeded very rapidly and with rather low stereoselectivity, even at –30 °C (Scheme 2). Separation of the diastereoisomeric amino alcohols was not attempted, as the two diastereoisomers (*anti,anti*-**4** and *anti,syn*-**4**) again had very similar R_F values, and were expected to give the same enol ethers **6** at the end of the synthesis (see below).

Earlier work had shown that the homoallylic amines **7** were best isolated as their hydrochloride salts.[2] The acidic conditions involved in this isolation are incompatible with the acid-labile enol ether function present in the products **6**. The amino alcohols **4** were, therefore, protected as their *N*-acetyl derivatives **5**. Reaction with acetic anhydride was totally chemoselective for the primary branched chain amine in the presence of a secondary alcohol, provided that the reaction was carried out in the absence of base, and for the minimum time (Scheme 3). Longer exposure tended to give *O*-acetyl derivatives **11** as

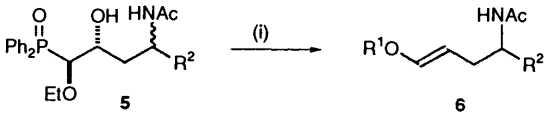


(i) Ac_2O, CH_2Cl_2, 1-2 h
4a, 5a: R^2 = Pr, 102%, 55:45
4b, 5b: R^2 = Ph, 70%, ratio not measured

Scheme 3

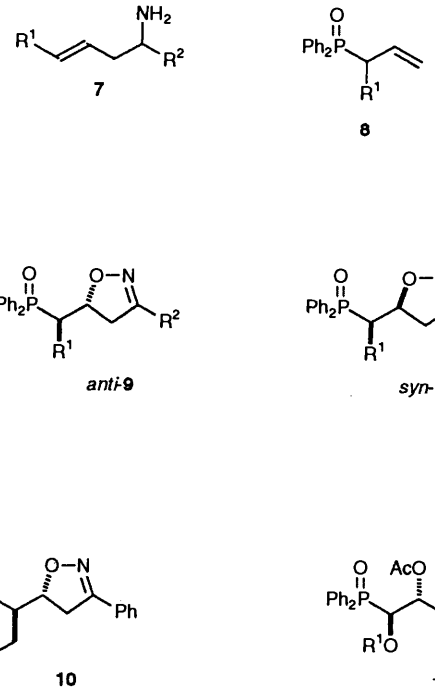
unwanted by-products. The diastereoisomers of *N*-acetylamino alcohols **5** (*anti*, *anti*-**5** and *anti*, *syn*-**5**) proved separable by flash column chromatography, although in this case such separation was unnecessary, and the relative stereochemistries of the two diastereoisomers were not determined.

Stereospecific elimination of diphenylphosphinic acid from *N*-acetylamino alcohols **5** proceeded as expected under our normal conditions of sodium hydride in *N,N*-dimethylformamide (DMF).[8] The hygroscopic enol ethers **6** could be purified by flash column chromatography without hydrolysis of the enol ether group, although some material was lost. Since the alcohols **5** were derived from isoxazolines *anti*-**3**, and therefore had *anti* stereochemistry across the two centres involved in the reaction, the stereospecific elimination was expected to give exclusively *E* alkenes (Scheme 4). The *E* geometry in alkenes **6**



(i) NaH, DMF
5a, 6a: R^2 = Pr, 91%
5b, 6b: R^2 = Ph, 39%

Scheme 4



was confirmed from the NMR spectra by the vicinal vinylic coupling constants of 12.6 and 12.7 Hz (typical values 6.5 for *Z* and 12.3 for *E* enol ethers).[9] Since the *N*-acetyl enol ethers **6** had only one chiral centre, the geometry of the third (N-bearing) centre in precursors **4** and **5** was unimportant, although the diastereoisomeric *N*-acetyl derivatives **5** could be separated if desired (see above).

The route shown in Scheme 1 thus represents the first synthesis of δ-amino enol ethers, which are produced as single geometrical isomers in a protected (*N*-acetylated) form. The stereochemistry of the double bond is directly related to the stereoselectivity in the nitrile oxide cycloaddition.

Experimental

General.—Column chromatography was carried out at slightly greater than atmospheric pressure using Merck Kieselgel 60 (230–400 mesh). High performance liquid chromatography (HPLC) was performed using a Dynamax prepacked silica column (21.4 mm i.d. × 25 cm), with a Gilson model 303 pump operating at 10 cm^3 min^{-1} and a Cecil Instruments CE 212A UV detection system measuring the absorbance at 254 nm. Thin layer chromatography (TLC) was carried out on commercially available pre-coated plates (Merck silica Kieselgel $60F_{254}$). All solvents were distilled before use. Tetrahydrofuran (THF) was freshly distilled from potassium using benzophenone radical as an indicator. Diethyl ether (Et_2O) was dried by distillation from calcium hydride. Dimethylformamide (DMF) was dried with and stored over activated molecular sieves (4 Å).

M.p.s were measured on a Reichart hot-stage microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 297 grating spectrophotometer. ^1H NMR spectra were recorded on Bruker WM 250 (250 MHz) and WM 400 (400 MHz) Fourier transform spectrometers. ^1H NMR spectra were recorded at 250 MHz unless otherwise stated. ^{13}C NMR were recorded on a Bruker WM 400 (100 MHz) spectrometer. Chemical shifts are quoted in ppm relative to tetramethylsilane (δ 0.00 ppm) or chloroform (δ 7.25 ppm) for proton spectra, and relative to chloroform (δ 77.0 ppm) for carbon spectra. *J* Values are given throughout in Hz. Mass spectra were recorded on an AEI Kratos MS30 machine using a DS503 data system

for high resolution analysis. Microanalyses were carried out using Carlo Erba 1106 or Perkin-Elmer 240 automatic analysers.

3-*Methoxy*-3-*diphenylphosphinoylprop*-1-*ene* **2a**.—By the method of Miller,[1] chlorodiphenylphosphine (3.3 cm^3, 18 mmol) in CH_2Cl_2 (4 cm^3) was added slowly to acrolein dimethyl acetal **1a** (2.2 cm^3, 18 mmol) at 0 °C under Ar. The mixture was stirred at 0 °C for 1 h and then at room temperature for 18 h. CH_2Cl_2 and MeCl were removed under reduced pressure to give the phosphine oxide **2a** as white needles (5.21 g, 105%), identified by its ^1H NMR spectrum: $\delta_H(CDCl_3)$ 3.33 (3 H, s, Me), 4.48 (1 H, tdd, *J* 1.3, 6.6 and 13.1, PCH), 5.34 (1 H, ddd, *J* 1.5, 3.1 and 10.1, CH=C$H_{cis}$$H_{trans}$), 5.35 (1 H, ddd, *J* 1.4, 4.2 and 17.5, CH=CH$_{cis}$$H_{trans}$), 5.86 (1 H, dddd, *J* 3.7, 6.5, 10.3 and 17.5, C*H*=CH$_{cis}$$H_{trans}$), 7.36–7.56 (6 H, m, Ph_2PO) and 7.69–7.93 (4 H, m, Ph_2PO).

3-*Diphenylphosphinoyl*-3-*ethoxyprop*-1-*ene* **2b**.—Chlorodiphenylphosphine (1.8 cm^3, 10 mmol) in CH_2Cl_2 (2 cm^3) was added dropwise at 0 °C under Ar to stirred acrolein diethyl acetal **1b** (1.5 cm^3, 10 mmol) and the mixture stirred at 0 °C to room temperature for 16 h. CH_2Cl_2 and EtCl were removed under reduced pressure to give 3-diphenylphosphinoyl-3-ethoxyprop-1-ene **2b** as a yellow oil, contaminated with chlorodiphenylphosphine oxide: the compound was characterised and used impure (Found: M^+, 286.1117. $C_{17}H_{19}O_2P$ requires *M*, 286.1123); R_F (EtOAc) 0.40; $\nu_{max}(CDCl_3)/cm^{-1}$ 3300–2750 (CH), 1590 and 1540 (Ph), 1415 (P–Ph), and 1175 (P=O); $\delta_H(CDCl_3)$ 1.09 (3 H, t, *J* 7.0, Me) 3.29 (1 H, qd, *J* 7.0 and 9.2, OC$H_A$$H_B$), 3.64 (1 H, qd, *J* 7.0 and 9.2, OCH$_A$$H_B$), 4.59 (1 H, dd, *J* 6.2 and 14.2, PCH), 5.27–5.40 (2 H, m, CH=CH_2), 5.89 (1 H, dddd, *J* 3.9, 6.3, 10.3 and 17.0, C*H*=CH$_2$) and 7.34–7.97 (10 H and signals from Ph_2POCl, m, Ph_2PO); *m*/*z* 286 (M^+, 4%), 271 (M^+ – Me, 7), 257 (M^+ – Et, 10), 242 [$Ph_2P(O)C_3H_5$, 10], 230 [$Ph_2P(O)Et$, 5], 202 (Ph_2PHO, 38), 201 (Ph_2PO, 92), 85 (M^+ – Ph_2PO, 100) and 77 (Ph, 46).

anti-5-[*Diphenylphosphinoyl*(*methoxy*)*methyl*]-3-*propyl*-4,5-*dihydroisoxazole* **3a**.—3-Diphenylphosphinoyl-3-methoxyprop-1-ene **2a** (274 mg, 1 mmol), butyraldehyde oxime (0.17 cm^3, 2 mmol), CH_2Cl_2 (10 cm^3) and NaOCl (2 mol dm^{-3} aqueous solution; 1.5 cm^3, 3 mmol) were stirred together for 17 d, with more oxime and NaOCl added after 4 and 6 d. The mixture was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on SiO_2, eluting with EtOAc–hexane (9:1) to give a mixture of diastereoisomeric 4,5-dihydroisoxazoles **3a** as a yellow oil which slowly crystallised. The anti-4,5-*dihydroisoxazole anti*-**3a** was purified by fractional crystallisation from EtOAc–hexane as white needles (96 mg, 27%), m.p. 133–135 °C (Found: C, 67.1; H, 6.7; N, 4.2%; M^+ + H, 358.1565. $C_{20}H_{24}NO_3P$ requires C, 67.2; H, 6.8; N, 3.9%; *M* + H, 358.1572); R_F (EtOAc) 0.32; $\nu_{max}(CDCl_3)/cm^{-1}$ 3100–3020 (aryl CH), 3000–2800 (CH), 1710 (C=N), 1595 (Ph), 1430 (P–Ph), 1190 (P=O), and 1110 (C–O); $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 7.4, CH_2*Me*), 1.49 (2 H, sextet, *J* 7.4, CH_2Me), 2.22 (2 H, t, *J* 7.5, 3′-H_2), 2.57 (1 H, dd, *J* 11.1 and 17.3, 4-$H_A$$H_B$), 2.90 (1 H, dd, *J* 8.6 and 17.4, 4-H$_A$$H_B$), 3.43 (3 H, s, MeO), 4.47 (1 H, dd, *J* 1.2 and 8.4, PCH), 4.97 (1 H, tdd, *J* 1.3, 8.8 and 10.7, 5-H), 7.45–7.60 (6 H, m, Ph_2PO), and 7.80–7.96 (4 H, m, Ph_2PO); $\delta_C(CDCl_3)$ 13.6 (CH_2*Me*), 19.6 (CH_2), 29.4 (CH_2), 36.4 (CH_2), 62.5 (d, *J* 8, MeO), 79.3 (d, *J* 11, C-5), 80.6 (d, *J* 85, PCH), 128.4, 128.5, 128.8, 128.9, 129.8 (d, *J* 97, *ipso*-C), 130.9, 131.0, 131.4 (d, *J* 94, *ipso*-C), 131.9, 132.0, 132.2, 132.3 and 160.0 (C=N); *m*/*z* 358 (M^+ + H, 1%), 288 (M^+ – PrCN, 3), 273 [$Ph_2P(O)C_3H_4O_2$, 9], 258 [$Ph_2P(O)C_3H_5O$, 31], 246 [$Ph_2P(O)C_2H_5O$, 82], 231 [$Ph_2P(O)CH_2O$, 100], 202 (Ph_2PHO, 17), 201 (Ph_2PO, 47), 185 (Ph_2P, 31) and 77 (Ph, 28).

anti-5-[*Diphenylphosphinoyl*(*methoxy*)*methyl*]-3-*phenyl*-4,5-*dihydroisoxazole* **3b**.—NaOCl (2 mol dm^{-3} aqueous solution; 1.5 cm^3, 3 mmol) was added to a stirred solution of 3-diphenylphosphinoyl-3-methoxyprop-1-ene **2a** (273 mg, 1 mmol) and benzaldehyde oxime (0.17 cm^3) in CH_2Cl_2 (10 cm^3) and the mixture stirred for 7 d, with more oxime and bleach added after 4 d. The mixture was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on SiO_2, eluting with 10% hexane in EtOAc to give a 3:1 mixture of the diastereoisomeric isoxazolines **3b** (259 mg, 66%), from which the anti-*isoxazoline anti*-**3b** was obtained by repeated recrystallisation from EtOAc–hexane as white plates (200 mg, 51%), m.p. (EtOAc–hexane) 118–120 °C (Found: M^+ – PhC_2H_3N, 273.0664. $C_{23}H_{22}NO_3P$ requires *M* – PhC_2H_3N, 273.0680); R_F (EtOAc) 0.43; $\nu_{max}(CDCl_3)/cm^{-1}$ 3060 (aryl CH), 2980–2800 (CH), 1670 (C=N), 1570 and 1490 (Ph), 1435 (P–Ph), 1190 (P=O) and 1115 (CO); $\delta_H(CDCl_3)$ 2.97 (1 H, dd, *J* 11.2 and 17.0, 4-$H_A$$H_B$), 3.32 (1 H, dd, *J* 9.4 and 16.8, 4-H$_A$$H_B$), 3.44 (3 H, s, MeO), 4.58 (1 H, dd, *J* 1.2 and 8.8, PCH), 5.18 (1 H, tdd, *J* 1.5, 9.3 and 11.0, 5-H), 7.34–7.70 (10 H, m, Ph_2PO and PhCN) and 7.79–8.00 (5 H, m, Ph_2PO and PhCN); $\delta_C(CDCl_3)$ 34.3 (CH_2), 62.6 (d, *J* 8, MeO), 80.4 (d, *J* 73, PCH), 80.9 (C-5), 126.6, 128.5, 128.6, 128.9, 129.3 (NC–C_{aryl}), 129.7 (d, *J* 96, *ipso*-C), 130.0, 131.0, 131.1, 131.2 (d, *J* 97, *ipso*-C), 132.0, 132.1, 132.4 and 157.6 (C=N); *m*/*z* 288 (M^+ – PhCN, 1%), 273 (M^+ – PhC_2H_3N, 4), 246 [$Ph_2P(O)CH_2OMe$, 100], 231 [$Ph_2P(O)CH_2O$, 85], 202 (Ph_2PHO, 17), 201 (Ph_2PO, 44) and 77 (Ph, 44).

anti-5-[*Diphenylphosphinoyl*(*methoxy*)*methyl*]-3-*phenyl*-4,5-*dihydroisoxazole* **3b**.—This compound was also made with sonication. By this method, 3-diphenylphosphinoyl-3-methoxyprop-1-ene **2a** (915 mg, 3.4 mmol), benzaldehyde oxime (0.51 cm^3, 6 mmol), CH_2Cl_2 (30 cm^3) and NaOCl (2 mol dm^{-3} aqueous solution; 3.5 cm^3, 7 mmol) were sonicated for 6.5 h. The mixture was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on SiO_2, eluting with EtOAc to give a mixture of the diastereoisomeric *isoxazolines* **3b** (685 mg, 52%).

anti-5-[*Diphenylphosphinoyl*(*ethoxy*)*methyl*]-3-*propyl*-4,5-*dihydroisoxazole* **3c**.—3-Diphenylphosphinoyl-3-ethoxyprop-1-ene **2b** (0.90 g, 3.15 mmol), butyraldehyde oxime (0.37 cm^3, 6.3 mmol), CH_2Cl_2 (30 cm^3) and NaOCl (2 mol dm^{-3} aqueous solution; 4 cm^3, 8 mmol) were stirred for 6 d, with more oxime and NaOCl added after 1 and 5 d. The mixture was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on SiO_2, eluting with EtOAc–hexane (3:2) and then EtOAc to give a mixture of diastereoisomeric 4,5-dihydroisoxazoles **3c** (731 mg, 63%). The anti-4,5-*dihydroisoxazole* was purified by fractional crystallisation from MeOAc–hexane as white needles (514 mg, 44%), m.p. 129–135 °C (Found: C, 67.8; H, 7.2; N, 3.5%; M^+ – C_2H_4O, 327.1394. $C_{21}H_{26}NO_3P$ requires C, 67.9; H, 7.0; N, 3.8%; *M* – C_2H_4O, 327.1388); R_F (EtOAc) 0.43; $\nu_{max}(CDCl_3)/cm^{-1}$ 3100–3020 (aryl CH), 3000–2800 (CH), 1615 (C=N), 1590 (Ph), 1430 (P–Ph), 1180 (P=O) and 1110 (CO); $\delta_H(CDCl_3)$ 0.89 [3 H, t, *J* 7.4, $(CH_2)_2$*Me*], 0.98 (3 H, t, *J* 7.0, OCH_2*Me*), 1.48 (2 H, sextet, *J* 7.3, CH_2CH_2Me), 2.21 (2 H, t, *J* 7.6, 3′-H_2), 2.56 (1 H, dd, *J* 11.0 and 17.2, 4-$H_A$$H_B$), 2.93 (1 H, dd, *J* 8.6 and 17.3, 4-H$_A$$H_B$), 3.37 (1 H, quintet, *J* 7.2, OC$H_A$$H_B$), 3.77 (1 H, quintet, *J* 7.2, OCH$_A$$H_B$), 4.53 (1 H, br d, *J* 8.6, PCH), 4.96 (1 H, br t, *J* 9.7, 5-H), 7.45–7.59 (6 H, m, Ph_2PO) and 7.80–7.97 (4 H, m, Ph_2PO); $\delta_C(CDCl_3)$ 13.6 (Me), 15.5 (Me), 19.6 (CH_2-CH_2Me), 29.4 (C-3′), 36.6 (C-4), 70.0 (d, *J* 7, OCH_2), 79.3

(d, *J* 12, C-5), 79.3 (d, *J* 85, PCH), 128.3, 128.4, 128.7, 128.8, 129.8 (d, *J* 97, *ipso* C), 131.0, 131.1, 131.3 (d, *J* 96, *ipso* C), 132.0, 132.1, 132.2 and 159.9 (C=N); *m/z* 327 ($M^+ - C_2H_4O$, 1.9%), 302 ($M^+ - PrCN$, 1.1), 286 ($M^+ - PrCNO$, 0.2), 273 [$Ph_2P(O)C_4H_8O$, 12], 260 [$Ph_2P(O)C_3H_7O$, 67], 258 ($M^+ - PrCN-C_2H_4O$, 11), 243 [$Ph_2P(O)C_2H_2O$, 9.3], 231 [$Ph_2P(O)CH_2O$, 100], 202 (Ph_2PHO, 23), 201 (Ph_2PO, 55), 185 (Ph_2P, 27), 170 ($M^+ - Ph_2PO$, 2.7) and 77 (Ph, 25).

anti-5-[*Diphenylphosphinoyl(ethoxy)methyl*]-3-*phenyl*-4,5-*dihydroisoxazole* **3d**.—3-Diphenylphosphinoyl-3-ethoxyprop-1-ene **2b** (0.90 g, 3.15 mmol), benzaldehyde oxime (0.762 g, 6.3 mmol), CH_2Cl_2 (30 cm^3) and NaOCl (2 mol dm^{-3} aqueous solution; 4 cm^3, 8 mmol) were stirred for 3 d, with more oxime and NaOCl added after 1 d. The mixture was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography on SiO_2, eluting with EtOAc–hexane (3–2) to give a mixture of diastereoisomeric 4,5-dihydroisoxazoles **3d** (800 mg, 63%). The anti-4,5-*dihydroisoxazole* was purified by fractional crystallisation from MeOAc–hexane as white needles (530 mg, 42%), m.p. 172–174 °C (Found: $M^+ - C_2H_4O$, 361.1221. $C_{24}H_{24}NO_3P$ requires $M - C_2H_4O$, 361.1210); R_F (EtOAc) 0.53; $\nu_{max}(CDCl_3)/cm^{-1}$ 3110–3000 (aryl CH), 3000–2800 (CH), 1590 and 1570 (Ph), 1430 (P–Ph), 1260 (CO), 1170 (P=O), 1115 (CO) and 1060 (CO); $\delta_H(CDCl_3)$ 0.94 (3 H, t, *J* 7.0, Me), 2.97 (1 H, dd, *J* 11.2 and 16.8, 4-H_AH_B), 3.36 (1 H, dd, *J* 9.0 and 17.5, 4-H_AH_B), 3.4 (1 H, qd, *J* 7.0 and 8.8, OCH_AH_B), 3.78 (1 H, qd, *J* 7.1 and 9.0, OCH$_A$$H_B$), 4.64 (1 H, br d, *J* 8.8, PCH), 5.17 (1 H, br dd, *J* 9.5 and 10.6, OC-5H), 7.29–7.39 (3 H, m, Ph_2PO and PhCN), 7.46–7.63 (8 H, m, Ph_2PO and PhCN) and 7.85–8.02 (4 H, m, Ph_2PO and PhCN); $\delta_C(CDCl_3)$ 15.4 (Me), 34.4 (C-4H_2), 70.7 (d, *J* 7, OCH_2), 79.0 (d, *J* 85, PCH), 80.8 (d, *J* 12, C-5), 126.6, 128.4, 128.5, 128.6, 128.8, 128.9, 129.2, 129.7 (d, *J* 97, *ipso* C), 130.0, 131.1, 131.2, 131.2 (d, *J* 96, *ipso* C), 132.1, 132.2, 132.3 and 157.6 (C=N); *m/z* 361 ($M^+ - C_2H_4O$, 0.7), 302 ($M^+ - PhCN$, 1.1), 273 [$Ph_2P(O)C_4H_8O$, 7.8], 260 [$Ph_2P(O)C_3H_7O$, 93], 243 [$Ph_2P(O)C_2H_2O$, 6.7], 231 [$Ph_2P(O)CH_2O$, 100], 201 (Ph_2PO, 42) and 77 (Ph, 31).

anti, anti- *and* anti, syn-4-*Amino*-1-*diphenylphosphinoyl*-1-*ethoxyheptan*-2-*ol* **4a**.—$NaBH_4$ (250 mg, 6.5 mmol) was added **portionwise** to a stirred solution of *anti*-5-[diphenylphosphinoyl-(ethoxy)methyl]-3-propyl-4,5-dihydroisoxazole **3c** (482 mg, 1.23 mmol) and $NiCl_2 \cdot 6H_2O$ (618 mg, 2.6 mmol) in MeOH (50 cm^3) at −30 °C under N_2 or Ar, and the mixture stirred for 5–10 min. The MeOH was removed under reduced pressure and NH_3 (aqueous solution, *d* 0.88; 40 cm^3) and CH_2Cl_2 (40 cm^3) were added, and the mixture was stirred under air until the organic layer was a pale yellow–brown. The mixture was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 40 cm^3). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure to give the amino alcohols **4a** as a 1 : 1 mixture of two diastereoisomers **A** and **B** (476 mg, 98%) as a yellow oil (Found: M^+, 375.1991. $C_{21}H_{30}NO_3P$ requires *M*, 375.1964); R_F (CH_2Cl_2–MeOH–NH_3, 100:10:2) 0.41; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3650 (NH_2), 3500–2970 (OH), 2970–2690 (CH), 1580 (Ph), 1460–1420 (P–Ph), 1170 (P=O), 1110 and 1090 (CO); $\delta_H(CDCl_3)$ 0.82 [3 HA or **B**, t, *J* 6.8 $(CH_2)_2Me$], 0.85 [3 HA or **B**, t, *J* 6.9, $(CH_2)_2Me$], 0.99 (3 HA or **B**, t, *J* 7.0, OCH_2Me), 1.00 (3 HA or **B**, t, *J* 7.0, OCH_2Me), 1.13–1.28 (4 HA or **B**, m, CH_2CH_2), 1.38 (1 HA or **B**, td, *J* 10.7 and 14.3, 4-H_AH_B), 1.54 (1 HA or **B**, ddd, *J* 2.8, 8.3 and 14.0, 4-H_AH_B), 1.62–1.72 (1 HA and **B**, m, 4-H_AH_B), 2.75 (1 HA or **B**, m, NCH), 3.12 (1 HA or **B**, m, NCH), 3.17 (1 HA or **B**, qd, *J* 7.1 and 8.9, OCH_AH_B), 3.21 (1 HA or **B**, qd, *J* 7.1 and 9.0, OCH_AH_B), 3.64 (1 HA or **B**, qd, *J* 7.0 and 8.9, OCH$_A$$H_B$), 3.74 (1 HA or **B**, qd, *J* 7.0 and 9.0, OCH$_A$$H_B$), 4.01 (1 HA or **B**, t, *J* 6.4, PCH), 4.09 (1 HA or **B**, dd, *J* 4.1 and 7.3, PCH), 4.29 (1 HA and **B**, m, HOC*H*), 7.40–7.55 (6 HA and **B**, m, Ph_2PO), 7.70–7.88 (2 HA and **B**, m, Ph_2PO) and 7.95–8.05 (2 HA and **B**, m, Ph_2PO); $\delta_C(CDCl_3)$ 13.9 (Me), 14.0 (Me), 15.3 (Me), 15.4 (Me), 18.7 (CH_2), 19.1 (CH_2) 37.8 (CH_2), 37.9 (CH_2), 39.3 (CH_2), 42.2 (CH_2), 46.0 (NC), 51.7 (NC), 68.9 (OCH), 70.2 (d, *J* 8, OCH_2), 70.3 (d, *J* 6, OCH_2), 72.8 (d, *J* 8, OCH), 82.8 (d, *J* 85, PCH), 82.9 (d, *J* 87, PCH), 128.1, 128.2, 128.4, 128.4, 128.5, 128.5, 129.9 (d, *J* 96, *ipso* C), 130.6 (d, *J* 95, *ipso* C), 131.2, 131.3, 131.8, 131.9, 132.1, 132.2, 132.3, 132.4 and 133.0; *m/z* 375 (M^+, 0.8%), 332 ($M^+ - Pr$, 1.2), 330 ($M^+ - EtO$, 0.5), 328 ($M^+ - C_2H_7O$, 1.6), 314 ($M^+ - C_3H_9O$, 3.2), 304 [$Ph_2P(O)C_5H_{11}O_2$, 4.2], 289 [$Ph_2P(O)C_4H_8O_2$, 3.2], 287 ($M^+ - Pr - EtO$, 2.5), 260 [$Ph_2P(O)C_3H_7O$, 89], 231 [$Ph_2P(O)CH_2O$, 100], 215 [$Ph_2P(O)CH_2$, 9.5], 202 (Ph_2PHO, 40), 201 (Ph_2PO, 100), 185 (Ph_2P, 85), 174 ($M^+ - Ph_2PO$, 14) and 77 (Ph, 23).

anti, anti- *and* anti, syn-4-*Amino*-1-*diphenylphosphinoyl*-1-*ethoxy*-4-*phenylbutan*-2-*ol* **4b**.—By the above method, $NaBH_4$ (233 mg, 6 mmol) was added **portionwise** to a stirred solution of *anti*-[5-diphenylphosphinoyl(ethoxy)methyl]-3-phenyl-4,5-isoxazole **4d** (500 mg, 1.23 mmol) and $NiCl_2 \cdot 6H_2O$ (587 mg, 2.5 mmol) in MeOH (100 cm^3) at −30 °C under N_2 or Ar, and the mixture stirred for 5–10 min. The MeOH was removed under reduced pressure and NH_3 (aqueous solution, *d* 0.88; 40 cm^3) and CH_2Cl_2 (40 cm^3) were added, and the mixture was stirred under air until the organic layer was a pale yellow–brown. The mixture was separated and the aqueous layer extracted with CH_2Cl_2 (3 × 40 cm^3). The combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure to give a 3.5 : 1 mixture of the *amino alcohols* **4b A** and **B**, respectively, as a pale yellow foam (489 mg, 97%) (Found: M^+, 409.1785. $C_{24}H_{28}NO_3P$ requires *M*, 409.1806); R_F (CH_2Cl_2–MeOH–NH_3, 100:10:2) 0.49; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3520–3120 (OH and NH_2), 2970–2800 (CH), 1585 (Ph), 1160 (P=O) and 1110 and 1090 (CO); $\delta_H(CDCl_3$, 400 MHz) 0.96 (3 **HB**, t, *J* 7.0, Me), 0.97 (3 **HA**, t, *J* 7.0, Me), 1.82–2.00 (2 HA and **B**, m, 3-H_AH_B), 3.13 (1 **HA**, qd, *J* 7.0 and 8.7, OCH_AH_B), 3.16 (1 **HB**, m, OCH_AH_B), 3.57 (1 **HA**, qd, *J* 7.0 and 8.7, OCH$_A$$H_B$), 3.65 (1 **HB**, qd, *J* 7.0 and 8.7, OCH$_A$$H_B$), 3.94 (1 **HA**, t, *J* 6.5, PCH), 3.98–4.03 (2 **HB**, m, PCH and NCH), 4.20 (1 **HA**, dq, *J* 3.0 and 7.0, OCH), 4.27 (1 **HB**, m, OCH), 4.36 (1 **HA**, dd, *J* 3.6 and 8.8, NCH), 7.17–7.31 (6 HA and **B**, m, Ph_2PO and PhCN), 7.40–7.60 (7 HA and **B**, m, Ph_2PO and PhCN), 7.72–7.88 (1 HA and **B**, m, Ph_2PO and PhCN), and 7.93–8.05 (1 HA and **B**, m, Ph_2PO and PhCN); $\delta_C(CDCl_3)$ (only signals for **A** are clearly visible) 15.3 (Me), 41.4 (C-3), 52.1 (NC), 68.7 (d, *J ca.* 5, OCH), 70.1 (d, *J* 5, OCH_2), 82.6 (d, *J* 85, PCH), 125.8, 126.1, 127.0, 128.3, 128.5, 128.6, 131.2, 131.3, 132.0, 132.1, 132.2, 132.3, 132.4 and 145.4 (NC-C_{aryl}); *m/z* 409 (M^+, 12%), 304 ($M^+ - PhCH_2N$, 6.4), 260 [$Ph_2P(O)C_3H_7O$, 81], 245 [$Ph_2P(O)C_2H_4O$, 6.7], 231 [$Ph_2P(O)CH_2O$, 100], 215 [$Ph_2P(O)CH_2$, 8], 208 ($M^+ - Ph_2PO$, 13), 202 (Ph_2PHO, 31), 201 (Ph_2PO, 51), 185 (Ph_2P, 17), 120 (PhC_2H_5N, 23), 106 ($PhCH_3N$, 60) and 77 (Ph, 29).

anti, anti- *and* anti, syn-4-*Acetamido*-1-*diphenylphosphinoyl*-1-*ethoxyheptan*-2-*ol* **5a**.—Ac_2O (1 cm^3) was added to a stirred solution of *anti, anti-* and *anti, syn*-4-amino-1-diphenylphosphinoyl-1-ethoxyheptan-2-ol **4a** (79 mg, 0.21 mmol) in CH_2Cl_2 (2 cm^3) under Ar, and the mixture stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the residue purified by column chromatography on SiO_2, eluting with EtOAc and then 10% MeOH in EtOAc. The first fraction isolated contained one *amido alcohol* **5a A** (49.5 mg, 56.5%); the second fraction isolated contained the other *amido alcohol* **5a B** (40 mg, 45.5%). The isomers were identified by ^1H NMR, but it is not known which isomer is which. The two were combined for characterisation

and further reaction. The combined isomers were a white foam (Found: $M^+ + H$, 418.2175. $C_{23}H_{32}NO_4P$ requires $M + H$, 418.2147); R_F (10% MeOH in EtOAc) 0.36 and 0.28; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3500–3200 (OH and NH), 3000–2800 (CH), 1660 (C=O), 1515 (PPh_2), 1160 (P=O), 1120 and 1095 (CO); $\delta_H(CDCl_3)$ isomer **A**: 0.83 (3 H, t, *J* 7.0, Me), 1.00 (3 H, t, *J* 7.0, Me), 1.25–1.39 (4 H, m, $MeCH_2CH_2$), 1.64–1.73 (2 H, m, 3-H_2), 1.87 (3 H, s, COMe), 3.21 (1 H, qd, *J* 7.0 and 9.0, OCH_AH_B), 3.67 (1 H, qd, *J* 7.0 and 9.0, OCH_AH_B), 4.07–4.13 (3 H, m, NCH and PCHCHO), 6.10 (1 H, d, *J* 8.7, NH), 7.46–7.56 (6 H, m, Ph_2PO), 7.76–7.84 (2 H, m, Ph_2PO) and 7.84–8.00 (2 H, m, Ph_2PO); $\delta_H(CDCl_3)$ isomer **B**: 0.84 (3 H, t, *J* 7.2, MeO), 0.98 (3 H, t, *J* 6.7, Me), 1.20–1.29 (2 H, m, $MeCH_2$), 1.35–1.41 (2 H, m, $MeCH_2CH_2$), 1.55–1.64 (1 H, m, 3-H_AH_B), 1.88–2.00 (1 H, m, 3-H_AH_B), 1.91 (3 H, s, COMe), 3.10 (1 H, quintet, *J* 7.5, OCH_AH_B), 3.52 (1 H, quintet, *J* 7.7, OCH_AH_B), 3.85–3.95 (1 H, m) and 4.03–4.15 (2 H, m) (NCH and PCHCHO), 6.04 (1 H, br s, NH), 7.50–7.58 (6 H, m, Ph_2PO), 7.77–7.85 (2 H, m, Ph_2PO) and 7.95–8.03 (2 H, m, Ph_2PO); *m/z* 418 (MH^+, 0.7%), 356 ($M^+ - C_3H_9O$, 1), 260 [$Ph_2P(O)C_3H_7O$, 60], 231 [$Ph_2P(O)CH_2O$, 100], 216 ($M^+ - Ph_2PO$, 26), 202 (Ph_2PHO, 20), 201 (Ph_2PO, 31) and 77 (Ph, 20).

anti, anti- *and* anti, syn-4-*Acetamido*-1-*diphenylphosphinoyl*-1-*ethoxy*-4-*phenylbutan*-2-*ol* **5b**.—Ac_2O (2 cm^3) was added to a stirred solution of *anti, anti-* and *anti, syn*-4-amino-1-diphenylphosphinoyl-1-ethoxy-4-phenylbutan-2-ol **4b** (187 mg, 0.46 mmol) in CH_2Cl_2 (4 cm^3) under Ar, and the mixture stirred for 1.25 h at room temperature. The solvent was removed under reduced pressure and the residue purified by column chromatography on SiO_2, eluting with EtOAc then 10% MeOH in EtOAc and finally 20% MeOH in EtOAc to give the *amido alcohols* **5b** as a pale yellow foam (145 mg, 70%), from which crystallisation (MeOAc–hexane) gave a single (unidentified) isomer as white needles, m.p. 173.5–175 °C (Found: C, 69.2; H, 6.75; N, 3.15; M^+, 451.1922. $C_{26}H_{30}NO_4P$ requires C, 69.2; H, 6.7; N, 3.1; *M*, 451.1912); R_F (10% MeOH in EtOAc) 0.36; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3500–3300 (OH), 2980–2800 (CH), 1665 (C=O), 1500 (P–Ph), 1155 (P=O), and 1120 and 1100 (CO); $\delta_H(CDCl_3)$ 0.99 (3 H, t, *J* 7.0, CH_2Me), 1.94 (3 H, s, COMe), 1.92–2.20 (2 H, m, 3-H_2), 3.19 (1 H, qd, *J* 7.0 and 8.7, OCH_AH_B), 3.64 (1 H, qd, *J* 7.0 and 9.0, OCH_AH_B), 4.04–4.10 (2 H, m, OCH and PCH), 5.21 (1 H, dt, *J* 3.5 and 8.5, NCH), 6.76 (1 H, d, *J* 8.3, NH), 7.14–7.28 (5 H, m, PhC), 7.40–7.57 (6 H, m, Ph_2PO) and 7.76–7.99 (4 H, m, Ph_2PO); $\delta_C(CDCl_3)$ 15.5 (CH_2Me), 22.6 (CO*Me*), 40.8 ($PhCCH_2$), 51.2 (NCH), 69.1 (d, *J* 8, OCH), 71.3 (d, *J* 6, OCH_2), 84.1 (d, *J* 85, PCH), 127.4, 128.1, 128.2, 128.3, 129.5, 129.5, 129.6, 129.8, 130.0, 131.3 (d, *J* 98, *ipso* to P), 132.1 (half of C *ipso* to P), 132.2, 132.3, 132.8, 133.0, 133.1, 133.5, 133.5, 144.1 (*ipso* to C) and 172.8 (C=O); *m/z* 451 (M^+, 0.9%), 289 [$Ph_2P(O)C_4H_8O_2$, 0.5], 260 [$Ph_2P(O)C_3H_7O$, 15], 231 [$Ph_2P(O)CH_2O$, 28], 202 (Ph_2PHO, 10), 201 (Ph_2PO, 10), 135 (PhC_3H_6O, 100) and 129 ($C_6H_{11}NO_2$, 100).

(E)-N-(1-*Ethoxyhept*-1-*en*-4-*yl*)*acetamide* **6a**.—NaH (50% dispersion in oil; 20 mg, 0.42 mmol) was added to a stirred solution of *anti, anti-* and *anti, syn*-4-acetamido-1-diphenylphosphinoyl-1-ethoxyheptan-2-ol **5a** (80 mg, 0.21 mmol) in DMF (3 cm^3) under Ar and the solution stirred for 17 h. Et_2O (20 cm^3) was added to the mixture which was then washed with 2.2 mol dm^{-3} aqueous NaOH (3 × 20 cm^3). The combined aqueous layers were washed with Et_2O (25 cm^3) and the combined organic layers dried (Na_2SO_4) and evaporated under reduced pressure. The residue (34.5 mg, 91%) was purified by column chromatography on SiO_2, eluting with EtOAc–hexane (4:1) to give the *enol ether* **6a** as white plates, m.p. 34–36 °C (Found: M^+, 199.1585. $C_{11}H_{21}NO_2$ requires *M*, 199.1572); R_F (EtOAc–hexane; 4:1) 0.28; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3470 (NH), 3000–2800 (CH), 1660 (C=O), 1505 and 1375 (alkyl chain), 1200–1120 (CO), and 930 (CH=CH trans); $\delta_H(CD_2Cl_2$, 400 MHz) 0.89 [3 H, t, *J* 6.8 $(CH_2)_2Me$], 1.23 (3 H, t, *J* 7.0, OCH_2Me), 1.26–1.38 (4 H, m, $MeCH_2CH_2$), 1.90 (3 H, s, COMe), 1.99–2.08 (2 H, m, $C{=}CCH_2$), 3.69 (2 H, q, *J* 7.0, OCH_2), 3.83 (1 H, m, NCH), 4.67 (1 H, td, *J* 7.7 and 12.6, OC=CH), 5.33 (1 H, m obscured by CH_2Cl_2, NH), and 6.23 (1 H, d, *J* 12.6, OCH=C); $\delta_C(CD_2Cl_2)$ 14.0 (Me), 14.8 (Me), 19.4 (CH_2), 23.4 (CO*Me*), 33.2 (CH_2), 36.4 (CH_2), 49.3 (NCH), 64.9 (OCH_2), 99.2 (OC=*C*), 148.2 (O*C*=C) and 160.3 (C=O); *m/z* 199 (M^+, 0.05%), 140 ($M^+ - MeCONH_2$, 30), 114 ($C_6H_{12}NO$, 16), 111 ($M^+ - MeCONH_2 - Et$, 17), 86 ($C_5H_{10}O$, 12), 84 (C_5H_8O, 18) and 72 (C_4H_8O, 100).

(E)-N-(4-*Ethoxy*-1-*phenylbut*-3-*enyl*)*acetamide* **6b**.—NaH (50% dispersion in oil; 20 mg, 0.5 mmol) was added to a stirred solution of *anti, anti-* and *anti, syn*-4-acetamido-1-diphenylphosphinoyl-1-ethoxy-4-phenylbutan-2-ol **5b** (118 mg, 0.26 mmol) in DMF (4 cm^3) under Ar, and the mixture stirred for 16 h. Et_2O (25 cm^3) was added to the mixture which was then washed with 2.2 mol dm^{-3} aqueous NaOH (3 × 25 cm^3). The combined aqueous layers were extracted with Et_2O (25 cm^3), and this organic extract washed with NaOH (2.2 mol dm^{-3}; 25 cm^3). The combined Et_2O layers were dried (Na_2SO_4) and evaporated under reduced pressure to give a yellow, hygroscopic solid, which was purified by column chromatography on SiO_2, eluting with 20% hexane in EtOAc to give the *enol ether* **6b** (24 mg, 39%) as white prisms, m.p. 79–82 °C (Found: $M^+ - C_2H_5NO$, 174.1050. $C_{14}H_{19}NO_2$ requires $M - C_2H_5NO$, 174.1045); R_F (20% hexane in EtOAc) 0.30; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3440 (NH), 3050–2800 (CH), 1660 (C=O), 1500 (Ph), 1195, 1160 and 1130 (CO) and 935 (CH=CH *trans*); $\delta_H(CD_2Cl_2)$ 1.21 (3 H, t, *J* 7.0, CH_2Me), 1.95 (3 H, s, COMe), 2.37 (2 H, dt, *J* 1.0 and 7.0, $NCCH_2$), 3.65 (2 H, q, *J* 7.0, OCH_2), 4.56 (1 H, td, *J* 7.6 and 12.6, OCH=C*H*), 4.88 (1 H, br q, *J* 7, NCH), 6.01 (1 H, br d, *J* 5.5, NH), 6.36 (1 H, br d, *J* 12.7, OCH) and 7.21–7.37 (5 H, m, Ph); $\delta_C(CD_2Cl_2)$ 14.7 (CH_2Me), 23.3 (CO*Me*), 35.1 ($NCCH_2$), 53.8 (NCH), 64.9 (OCH_2), 98.7 (OC=*C*), 126.6, 127.2 and 128.6 (*o*, *m* and *p* Cs), 142.6 (*ipso* C), 148.6 (O*C*=C) and 169.3 (C=O); *m/z* 174 ($M^+ - C_2H_5NO$, 18%), 148 (PhC_3H_5NO, 32), 106 ($PhCH_3N$, 100) and 57 (C_2H_3NO, 16).

References

1 M. Maleki, A. Miller and O. W. Lever, *Tetrahedron Lett.*, 1981, **22**, 365.
2 S. K. Armstrong, E. W. Collington, J. G. Knight, A. Naylor and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1993, 1433.
3 D. R. Borthakur and J. S. Sandhu, *J. Chem. Soc., Chem. Commun.*, 1988, 1444.
4 (*a*) K. N. Houk, S. R. Moses, Y.-D. Wu, N. G. Rondan, V. Jäger, R. Schohe and F. R. Fronczek, *J. Am. Chem. Soc.*, 1984, **106**, 3880; (*b*) K. N. Houk, H.-Y. Duh, Y.-D. Wu and S. R. Moses, *J. Am. Chem. Soc.*, 1986, **108**, 2754.
5 D. P. Curran, *J. Am. Chem. Soc.*, 1983, **105**, 5826; D. P. Curran and S. A. Gothe, *Tetrahedron*, 1988, **44**, 3945.
6 S. K. Armstrong, S. Warren, E. W. Collington and A. Naylor, *Tetrahedron Lett.*, 1991, **32**, 4171.
7 R. Annunziata, M. Cinquini, F. Cozzi, A. Gilardi and A. Restelli, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2289.
8 A. D. Buss and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2307; D. Cavalla, W. B. Cruse and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1883; A. D. Buss, N. Greeves, R. Mason and S. Warren, *J. Chem. Soc., Perkin Trans 1*, 1987, 2569.
9 P. Laszlo and P. von Schleyer, *Bull. Soc. Chim. Fr.*, 1964, 87.

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