The reaction of unstabilised 1,3,4-oxadiazolium-N-methanide 1,3-dipoles with alkenes: N-substituted Δ-2-pyrrolines: contrast with the 1,3,4-thiadiazolium analogue

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Dedicated to Tony McKervey on the occasion of his 65th birthday
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Abstract
Treatment of transient 2,5-diaryl-1,3,4-oxadiazolium-3-methanides, unstabilized 1,3-dipoles, at -60°C with acrylonitrile, methyl acrylate, dimethyl maleate, dimethyl fumarate, chloroacrylonitrile, dimethyl- and diethyl acetylenedicarboxylates, methyl propiolate and butyne-3-one gave in all cases a 1-N-benzamido-substituted pyrrole or pyrroline product. This contrasts with the corresponding 1,3,4-thiadiazolium-methanide 1,3-dipole where the cycloadducts were stable. The reactions involved cycloadditions followed by ring-opening through 1,2- or 1,4-conjugate elimination processes. An X-ray crystal structure is reported on 1-\{N-benzoyl-N-[Z-1,2-dimethoxycarbonylvinyl] amino\}-2-phenyl-3,4-dimethoxycarbonyl pyrrole, 17.

Keywords: 1,3-Dipolar cycloadditions, azolium-N-methanide, Δ-2-pyrrolines

Introduction

In our exploration of exocyclic azolium ylide systems as 1,3-dipoles which undergo interesting cycloaddition-rearrangement sequences we have recently established the transient 1,3,4-thiadiazolium-3-methanide species 5 as a synthon for the rare fused pyrrolo [2,1-b]-1,3,4-thiadiazole ring system 7 via low-temperature cycloaddition reactions with substituted alkenes. The cycloadducts 7 were stable products. Similar reactions with the oxadiazolium 1,3-dipole 6 should give oxygen analogues 8.

Results and Discussion
The species 5 was generated at -60°C from the salts 3 by treatment with CsF following a procedure originally developed with quaternised Schiff bases. Herein we have similarly generated the 1,3,4-oxadiazolium-3-methanide species 6 at -60°C in methylene chloride in the presence of a number of alkene dipolarophiles. The products of these reactions were the 1-N-benzamido-4,5-dihydro-pyrroles 9, 10, 11 (Scheme 1, Table) and curiously the bicyclic structure 8 proved labile under the reaction conditions even at -60°C (Scheme 1).

Scheme 1. Reagents: (i) trimethylsilylmethyl trifluoromethanesulfonate; (ii) CsF; (iii) mono- and 1,2-disubstituted alkenes; (iv) 1-chloroacrylonitrile. Some 13C NMR shifts* shown.
The rearrangement of the cycloadduct involves a 1,2-elimination along the C(7)-C(7a) bond in structure 8 which did not occur in structure 7. It seems that replacement of the S atom by the electronegative O atom in the fused bicyclic structure 8 has increased the acidity of the 7-C-H bond sufficiently that this 1,2-elimination occurred under the reaction conditions. These conditions may be important and the CsF present could be playing a role in the eliminative ring-opening. In the reactions of the thiadiazolium dipole 5 the stereochemistry of the cycloaddition was predominantly endo and the substituent Y and Z in the products 7 were endo to the fused bicyclic structure. For the dipoles 6 the stereochemistry is lost in situ in the second step and hence the same product is obtained from dimethyl maleate and dimethyl fumarate (Table, entries 3 and 4).

**Table. Products from the reactions of 1,3-dipoles 6a-6d**

<table>
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<tr>
<th>Entry</th>
<th>Dipolarophile</th>
<th>Ar</th>
<th>Cpd</th>
<th>Y</th>
<th>Z</th>
<th>Yield(%)</th>
<th>Mp/°C</th>
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<tr>
<td>1</td>
<td>Acrylonitrile</td>
<td>Ph</td>
<td>9</td>
<td>H</td>
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<td>H</td>
<td>CO₂Me</td>
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<td>CO₂Me</td>
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<td>11</td>
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<td>CO₂Me</td>
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<td>5</td>
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<td>-</td>
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<td>Ph</td>
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<td>18</td>
<td>-</td>
<td>-</td>
<td>58</td>
<td>gum&lt;sup&gt;c&lt;/sup&gt;</td>
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</table>

<sup>a</sup> Dimethyl- and Diethyl acetylenedicarboxylate.

<sup>b</sup> Recrystallised from dichloromethane-hexane (2:1 v/v).

<sup>c</sup> Sticky low-melting solids.
Interestingly in the reaction with 1-chloro-1-cyano ethene (chloroacrylonitrile) a double elimination occurred giving the aromatised product 12 (Scheme 1, Table entry 5). In this case, with Cl atom in place of the H-atom at C-7 of structure 8, an initial 1,2-elimination of HCl occurred along the C(6)-C(7) bond of 8 followed by a 1,4-conjugate elimination at the 5-C-H and 7a-C-O bonds giving an overall aromatisation. The intermediate from the initial HCl elimination would be the expected cycloadduct from an alkyne dipolarophile. As expected cycloadducts from alkyne dipolarophiles readily aromatised in situ giving the products 13a-13d, 14a-14d, 15a-15b and 16 (Scheme 2). When higher than five molar excess of dipolarophile was used in these reactions the amido N-H underwent a further nucleophilic addition across a molecule of the excess alkyne. This addition appears to be a four-centred cis-addition since the products had the structure 17 and 18 shown (Scheme 2, Figure 1). In a known stereo-electronic effect nucleophiles adding to triple bonds are expected to repel the π-electrons to form a lone pair oriented trans to the incoming nucleophile and the H-atom should ultimately bond at this trans-site. The cis-addition was confirmed by an X-ray crystal structure of compound 17 (Figure 1).

Scheme 2. Reagents: (i) CsF, alkyne dipolarophiles, (ii) dialkyl acetylenedicarboxylates. Some $^1$H and $^{13}$C* NMR shifts shown.

The structures of the products were established from microanalyses, i.e., proton and carbon-13 NMR spectra which showed all of the expected signals and splitting. The enamine unit of the non-aromatic Δ-2 pyrroline structure 9 showed the expected deshielding of the enamine α-carbon (C-2) to 162-166ppm as well as the expected shielding of the enamine β-carbon (C-3) to
101-103ppm (Scheme 1). Similar shielding effects were also present in the exocyclic enamine unit in products 17 and 18 (Scheme 2). When Z was a CN substituent in compound 9 the pyrroline C-3 was further shielded to 82ppm. The structural assignments and the reaction outlines are further supported by the X-ray crystal structure determination on compound 17 (Figure 1). The regiochemistry of the products indicates an initial HOMO-dipole controlled cycloaddition\(^8\) with the dipole CH\(-2\) terminus bonding to the dipolarophile unsubstituted terminus. The reactions described for the 1,3-dipole species \textbf{6a-6d} provide new routes to selectively substituted partially reduced pyrrole derivatives. Despite the range of known routes\(^9\) to the pyrrole ring there is still a need to find controllable new routes to special derivatives and in particular dihydro pyrroles because of the importance of partially reduced pyrroles as intermediates in natural product synthesis.\(^{9,10}\)

![Figure 1](image_url)  
*Figure 1. X-Ray crystal structure of compound 17.*

**Experimental Section**

**General Procedures.** Melting points were measured on a Stuart Scientific melting point apparatus. IR spectra were measured with a Perkin-Elmer Spectrum 1000 FT-IR spectrometer. NMR spectra were measured on a JEOL LAMBDA 400MHz instrument with tetramethylsilane
as an internal reference and deuteriochloroform as the solvent. J values are given in Hz. All carbon-13 NMR assignments were supported by DEPT. Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser. The following chemicals were purchased from Aldrich: acrylonitrile, methyl acrylate, dimethyl fumarate and methyl methacrylate; from Fluka, 1-chloroacrylonitrile; from Lancaster: dimethyl maleate (99%). Dichloromethane was refluxed over CaH₂, followed by distillation onto 4Å molecular sieves.

Synthesis of 2,5-Diphenyl-3-trimethylsilylmethyl-1,3,4-oxadiazolium trifluoromethanesulfonate (4a). A solution of 2,5-diphenyl-1,3,4-oxadiazole 2a (1.0g, 4.5mmol) and trimethylsilylmethyl trifluoromethanesulfonate (0.99cm³, 4.95mmol) in dry CH₂Cl₂ (10cm³) was stirred at 50°C under reflux condenser for 24 hrs., evaporated under reduced pressure and the white residue washed with diethyl ether to give 4a, m.p. 141-142°C (from CH₂Cl₂/diethyl ether) (2.04g, 99%) (Found: C, 49.7; H, 4.6; N, 6.1. C₁₉H₂₁F₃N₂O₄Si requires C, 49.7: H, 4.7; N, 6.1%); δH(CDCl₃) 0.27 (s, 9H, SiMe₃), 4.23 (s, 2H, N-CH₂), 7.57-7.82 (m, 6H, H-meta, para), 8.08 (d, 2H, J 7.3, H-ortho of C-5Ph), 8.17 (d, 2H, J 7.3, H-ortho of C-2Ph); δC(CDCl₃) –2.0 (SiMe₃), 44.1 (N-CH₂), 120.2, 135.7, 128.0, 130.0 (C-1', C-2', C-3', C-4' of C-2Ph), 117.3, 134.6, 129.6, 130.4 (C-1', C-2', C-3', C-4' of C-5Ph), 162.4 (C-5), 164.1 (C-2).

The salts 4b-4d were similarly prepared.

2,5-Di(4'-methylphenyl)-3-trimethylsilylmethyl-1,3,4-oxadiazolium trifluoromethanesulfonate (4b). M.p. 155-156°C (from CH₂Cl₂/diethyl ether) (99%) (Found: C, 51.7; H, 4.9; N, 5.5. C₂₁H₂₅F₃N₂O₄Si requires C, 51.8; H, 5.1; N, 5.6%); δH(CDCl₃) 0.25 (s, 9H, SiMe₃), 2.45, 2.47 (s, 3H each, 4'-Me), 4.21 (s, 2H, N-CH₂), 7.37, 7.48 (ds, 4H, 3'-CH of p-Tolyl rings), 7.96, 8.10 (ds, 4H, 2'-CH of p-Tolyl rings); δC(CDCl₃) –2.1 (SiMe₃), 21.7, 21.9 (4-Me), 43.9 (N-CH₂), 114.2, 116.9 (C-1'), 127.7, 130.2, 130.3 (C-2' and C-3' overlap), 145.7, 147.3 (C-4'), 161.9 (C-5), 163.7 (C-2).

2,5-Di(4'-methoxyphenyl)-3-trimethylsilylmethyl-1,3,4-oxadiazolium trifluoromethanesulfonate (4c). M.p. 156-157°C (from CH₂Cl₂/diethyl ether) (97%) (Found: C, 48.7; H, 4.8; N, 5.1. C₂₁H₂₅F₃N₂O₆Si requires C, 48.6; H, 4.8; N, 5.4%); δH(CDCl₃) 0.25 (s, 9H, SiMe₃), 3.89, 3.90 (s, 3H each, 4'-OMe), 4.19 (s, 2H, N-CH₂), 7.05, 7.17 (ds, 4H, 3'-CH of p-MeOC₆H₄ rings), 8.01, 8.20 (ds, 4H, 2'-CH of p-MeOC₆H₄ rings); δC(CDCl₃) –2.2 (SiMe₃), 55.6, 55.8 (4'-OMe), 43.8 (N-CH₂), 108.5, 111.7 (C-1'), 129.7, 132.6 (C-2'), 115.0, 115.6 (C-3'), 161.0, 162.9 (C-4'), 164.3 (C-5), 165.4 (C-2).

2,5-Di(4'-bromophenyl)-3-trimethylsilylmethyl-1,3,4-oxadiazolium trifluoromethanesulfonate (4d). Insolubility prevented recrystallisation of the gummy solid (68% yield) and measurement of NMR spectra. The crude sample was used directly to obtain the products 13d and 14d which were fully characterised.

(i) Reactions with Substituted Alkenes
1-N-Benzamido-2-phenyl-3-cyano-4,5-dihydropyrrole (9). A solution of the salt 4a (0.28g, 0.61mmol) and acrylonitrile (0.40cm³, 6.1mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 9, m.p. 178-179°C (from 2:1 v/v CH₂Cl₂/hexane)(92%) (Found: C, 74.4; H, 4.8; N, 14.0. C₁₈H₁₅N₃O requires C, 74.7; H, 5.2; N, 14.5%). i.r. νamax (nujol mull) cm⁻¹ 3304 (NH), 2197 (CN), 1651 (amido C=O); δH (CDCl₃) 2.84 (dd, 2H, J 9.4, 9.3, CH₂-4), 3.76 (dd, 2H, CH₂-5), 7.27-7.56 (m, 10H, H aromatic), 8.40 (s, 1H, amido NH); δC (CDCl₃) 28.9 (C-4), 54.2 (C-5), 82.1 (pyrrole C-3), 118.8 (CN), 132.2, 130.4, 127.9, 128.3 (C-1’, C-2’, C-3’, C-4’ of phenyl), 131.9, 128.5, 126.9, 128.3 (C-1’, C-2’, C-3’, C-4’ of phenyl), 165.2 (pyrrole C-2), 166.8 (amido C=O).

1-N-Benzamido-2-phenyl-3-methoxycarbonyl-4,5-dihydropyrrole (10). A solution of the salt 4a (0.28g, 0.61mmol) and methyl acrylate (0.55cm³, 6.1mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 10, a gum (77%) (recollected crude sample); i.r. νamax (nujol mull) cm⁻¹ 3177 (NH), 1734 (ester C=O), 1660 (amido C=O); δH (CDCl₃) 2.81 (dd, 2H, J 9.3, 9.5, CH₂-4), 3.50 (s, 3H, OMe), 3.65 (dd, 2H, CH₂-5), 7.14-7.38 (m, 10H, H aromatic), 8.55 (s, 1H, amido NH); δC (CDCl₃) 26.6 (C-4), 50.6 (OMe), 53.4 (C-5), 102.5 (pyrrole C-3), 132.3, 130.5, 127.0, 128.3 (C-1’, C-2’, C-3’, C-4’ of phenyl), 131.6, 129.1, 126.9, 128.3 (C-1’, C-2’, C-3’, C-4’ of phenyl), 162.2 (pyrrole C-2), 166.0 (ester C=O), 167.1 (amido C=O).

1-N-Benzamido-2-phenyl-3,4-dimethoxycarbonyl-4,5-dihydropyrrole (11). A solution of the salt 4a (0.28g, 0.61mmol) and dimethyl maleate (0.76cm³, 6.1mmol) or dimethyl fumarate (0.88g, 6.1mmol) from separate reactions in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 11, m.p. 131-132°C (from 2:1 v/v CHCl₃/hexane)(94% from dimethyl maleate, 85% from dimethyl fumarate) (Found: C, 66.3; H, 5.2; N, 7.3. C₂₁H₂₀N₂O₅ requires C, 66.3; H, 5.3; N, 7.4%). i.r. νamax (nujol mull) cm⁻¹ 3295 (NH), 1739 (ester C=O), 1682 (amido C=O); δH (CDCl₃) 3.33, 3.52 (s, 3H each, OMe), 3.62 (m, 1H, H-4 pyrrole), 3.94 (m, 2H, 5-CH₂ pyrrole), 7.10-7.30 (m, 10H, H aromatic); δC (CDCl₃) 45.6 (C-4), 50.6, 52.1 (OMe), 56.2 (C-5), 101.3 (pyrrole C-3), 131.8, 129.4, 126.9, 127.3 (C-1’, C-2’, C-3’, C-4’ of phenyl), 129.6, 128.3, 126.9, 129.1 (C-1’, C-2’, C-3’, C-4’ of phenyl), 163.6 (pyrrole C-2), 165.1, 167.1 (ester C=O), 174.0 (amido C=O).

1-N-Benzamido-2-phenyl-3-cyano pyrrole (12). A solution of the salt 4a (0.28g, 0.61mmol) and 1-chloro acrylonitrile (0.49cm³, 6.1mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated
with CsF (0.19 g, 1.22 mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 12, a gum (86%) (Found: C, 74.9; H, 4.2; N, 14.2. C₁₈H₁₃N₃O requires C, 75.2; H, 4.6; N, 14.6 %); i.r. ν max (nujol mull) cm⁻¹ 3247 (NH), 2224 (CN), 1671 amido C=O; δ H (CDCl₃) 6.49 (d, 1H, H-5 pyrrole ring), 6.36 (d, 1H, H-4 pyrrole ring), 7.22-7.33 (m, 6H, H meta,para ), 7.48-7.57 (m, 4H, H ortho ) 10.27 (s, 1H, amido NH); δ C (CDCl₃) 90.8 (pyrrole C-3), 110.4 (pyrrole C-4), 116.8 (CN), 123.8 (pyrrole C-5), 141.4 (pyrrole C-2), 133.0, 130.4, 127.4, 128.7 (C-1', C-2', C-3', C-4' of phenyl), 131.9, 129.4, 126.8, 128.6 (C-1', C-2', C-3', C-4' of phenyl), 167.2 (amido C=O).

(ii) Reactions with Substituted Alkynes

1-N-Benzamido-2-phenyl-3, 4-dimethoxycarbonyl pyrrole (13a). A solution of the salt 4a (0.28 g, 0.61 mmol) and dimethyl acetylenedicarboxylate (0.26 cm³, 2.14 mmol) in CH₂Cl₂ (10 cm³) was cooled to -60°C, treated with CsF (0.19 g, 1.22 mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in a 1% (v/v) changing gradient 100:0 to 95:5 gave 13a, m.p. 184-185°C (from 2:1 v/v CH₂Cl₂/hexane) (81%) (Found: C, 66.5; H, 5.2; N, 7.7. C₂₁H₁₈N₂O₅ requires C, 66.6; H, 4.8; N, 7.4 %); i.r. ν max (neat) cm⁻¹ 3250 (NH), 1733, 1712 ester C=O, 1661 amido C=O; δ H (CDCl₃) 3.62, 3.65 (s, 3H each, OMe), 7.08 (s, 1H, H-5 pyrrole ring), 7.26-7.52 (m, 6H, H meta,para of both phenyl rings), 7.70-7.72 (d, 2H, J 7.3 H ortho of phenyl ring), 10.24 (s, 1H, amido NH); δ C (CDCl₃) 51.6, 52.0 (OMe), 113.7 (pyrrole C-3), 113.9 (pyrrole C-4), 132.8 (pyrrole C-5), 137.0 (pyrrole C-2), 127.5, 128.0, 128.7, 128.9, 129.6, 130.7 (overlapping of C-aromatic signals), 164.3, 166.0 (ester C=O), 166.7 (amido C=O).

Compounds 13b-13d were prepared similarly and showed all the expected NMR signals.

1-N-Benzamido-2-phenyl-3, 4-diethoxycarbonyl pyrrole (14a). A solution of the salt 4a (0.28 g, 0.61 mmol) and diethyl acetylenedicarboxylate (0.34 cm³, 2.14 mmol) in CH₂Cl₂ (10 cm³) was cooled to -60°C, treated with CsF (0.19 g, 1.22 mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3 cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 14a, a gum (72%) (recollected crude sample); i.r. ν max (neat) cm⁻¹ 3266 (NH), 1721 (br) ester and amido C=O; δ H (CDCl₃) 1.07, 1.19 (t, 3H each, CH₃), 4.04, 4.11 (quartets, 2H each, OCH₂), 7.07 (s, 1H, H-5 pyrrole ring), 7.26-7.52 (m, 6H, H meta,para of both phenyl rings), 7.70-7.72 (m, 4H, H ortho of both phenyl rings), 10.24 (s, 1H, amido NH); δ C (CDCl₃) 51.6, 52.0 (OMe), 113.3 (pyrrole C-3), 113.6 (pyrrole C-4), 132.8 (pyrrole C-5), 137.0 (pyrrole C-2), 127.5, 128.0, 128.7, 128.9, 129.6, 130.7 (overlapping of C-aromatic signals), 164.3, 166.0 (ester C=O), 166.7 (amido C=O).

Compounds 14b-14d were prepared similarly and showed all the expected NMR signals.
1-N-Benzamido-2-phenyl-3-methoxycarbonyl pyrrole (15a). A solution of the salt 4a (0.28g, 0.61mmol) and methyl propiolate (0.54cm³, 6.1mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 15a, m.p. 130-132°C (from 2:1 v/v CH₂Cl₂/hexane) (89%) (Found: C, 71.1; H, 4.9; N, 8.3. C₁₉H₁₆N₂O₃ requires C, 71.2; H, 5.0; N, 8.7%); i.r. ν_max (nujol mull) cm⁻¹ 3243 (NH), 1708 ester C=O, 1649 amido C=O; δH (CDCl₃) 3.48 (s, 3H, OMe), 6.44 (d, 1H, J 2.9, H-4 pyrrole ring), 6.52 (d, 1H, H-5 pyrrole ring), 7.13-7.40 (m, 10H, H aromatic), 9.81 (s, 1H, amido NH); δC (CDCl₃) 51.0 (OMe), 109.2 (pyrrole C-4), 111.8 (pyrrole C-3), 132.5 (pyrrole C-5), 138.7 (pyrrole C-2), 131.0, 129.4, 122.4, 128.5 (C-1', C-2', C-3', C-4' of phenyl), 165.1 (ester C=O), 167.3 (amido C=O).

Compound 15b was prepared similarly and showed all the expected NMR signals.

1-N-Benzamido-2-phenyl-3-acetyl pyrrole (16). A solution of the salt 4a (0.28g, 0.61mmol) and 3-butyn-2-one (0.48cm³, 6.1mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 16, m.p. 90-92°C (from 2:1 v/v CH₂Cl₂/hexane) (76%) (recollected crude sample); i.r. ν_max (nujol mull) cm⁻¹ 3454 (NH), 1657 amido C=O; δH (CDCl₃) 1.86 (s, 3H, CH₃), 6.51 (m, 2H, H-4 and H-5 pyrrole ring), 7.13-7.19 (m, 8H, H-meta,para of both phenyls, Hortho of one phenyl), 7.43 (d, 2H, J 7.8, Hortho), 10.35 (s, 1H, amido NH); δC (CDCl₃) 28.5 (CH₃), 106.4 (pyrrole C-3), 108.4 (pyrrole C-3), 132.4 (pyrrole C-5), 138.6 (pyrrole C-2), 130.3, 129.9, 127.4, 128.0 (C-1', C-2', C-3', C-4' of phenyl), 131.0, 128.9, 127.5, 128.5 (C-1', C-2', C-3', C-4' of phenyl), 167.3 (amido C=O), 194.9 (C=O).

1-{N-Benzoyl-N-[Z-1,2-dimethoxycarbonylviny] amino}-2-phenyl-3,4-dimethoxycarbonyl pyrrole 17 (reaction from 5 molar excess of DMAD). A solution of the salt 4a (0.28g, 0.61mmol) and dimethyl acetylenedicarboxylate (0.37cm³, 3.05mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave 17, m.p. 186-188°C (from 2:1 v/v CH₂Cl₂/hexane) (64%) (Found: C, 62.2; H, 4.5; N, 5.7. C₂₇H₂₄N₂O₉ requires C, 62.3; H, 4.6; N, 5.4%); i.r. ν_max (nujol mull) cm⁻¹ 1719 (br) ester C=O, 1655 amido C=O; δH (CDCl₃) 3.67, 3.73, 3.76, 3.86 (s, 3H each, OMe), 5.38 (s, 1H, H-β), 7.05-7.38 (m, 10H, H aromat), 7.56 (s, 1H, H-5 pyrrole ring); δC(CDCl₃) 51.9, 52.1, 52.3, 53.3 (OMe), 109.8 (C-β), 114.9 (pyrrole C-4), 115.7 (pyrrole C-3), 132.7 (pyrrole C-5), 136.1 (pyrrole C-2), 145.6 (C-α), 130.6, 129.4, 125.8, 128.3 (C-1', C-2', C-3', C-4' of phenyl), 129.8,
128.6, 126.8, 128.6 (C-1’, C-2’, C-3’, C-4’ of phenyl), 162.1, 162.9, 164.4, 164.4 (ester C=O), 167.5 (amido C=O).

1-{N-Benzoyl-N-[Z-1,2-diethoxycarbonylvinyl] amino}-2-phenyl-3,4-diethoxycarbonyl pyrrole 18 (reaction with a 5 molar excess of DEAD). A solution of the salt 4a (0.28g, 0.61mmol) and diethyl acetylenedicarboxylate (0.49cm³, 3.05mmol) in CH₂Cl₂ (10cm³) was cooled to -60°C, treated with CsF (0.19g, 1.22mmol), stirred at -60°C for 5 days, warmed to ambient temperatures, filtered to remove salts, evaporated under reduced pressure and the residue in dichloromethane (3cm³) placed on a silica gel-60 column (230-400 mesh ASTM). Elution with a gradient mixture of dichloromethane and diethyl ether in the gradient 100:0 to 95:5 gave compound 18, a sticky gum (58%) (recolumned crude sample); i.r. ν max (nujol mull) cm⁻¹ 1724 (br) ester C=O; δ H (CDCl₃) 1.21-1.43 (m, 12H, 4 x CH₃), 4.15-4.38 (m, 8H, 4 x OCH₂), 5.47 (s, 1H, H-β), 7.14-7.59 (m, 10H, H aromatic), 7.61 (s, 1H, H-5 pyrrole ring); δ C (CDCl₃) 13.4, 13.6, 13.8, 14.1 (4 x CH₃), 60.2, 60.6, 60.9, 61.2 (4 x OCH₂), 111.1 (C-β), 114.0 (pyrrole C-3), 115.1 (pyrrole C-4), 132.5 (pyrrole C-5), 135.8 (pyrrole C-2), 145.0 (C-α), 132.0, 130.5, 127.0, 128.2 (C-1’, C-2’, C-3’, C-4’ of phenyl), 130.7, 129.5, 125.7, 128.1 (C-1’, C-2’, C-3’, C-4’ of phenyl), 161.4, 162.3, 163.9, 176.4 (ester C=O), 168.9 (amido C=O). Compound 14a (25%) was also recovered.

X-Ray Crystal structure data for compound (17)
The crystals were grown from dichloromethane/hexane (2:1 v/v) by slow evaporation to the atmosphere. The crystal used for data collection had the approximate dimensions 0.66 x 0.44 x 0.25 mm. The crystal was triclinic with the space group P-1 and had unit cell parameters a = 11.092(5), b = 11.205(3), c = 13.054(4) Å, α = 64.83(3), β = 65.75(3), γ = 69.92(3)°. Reflections were collected on an Enraf-Nonius CAD4F four circle diffractometer, using graphite monochromated Mo-Kα radiation, λ = 0.71069Å. The criterion which qualified a reflection for observation was I > 2σ(I) and 2245 reflections satisfied this condition. The calculated density was 1.319Mg/m³ and Z = 2. The absorption coefficient was 0.100 mm⁻¹ and the theta range for data collection was 1.81 to 20.86°. The total number on independent reflections was 2512 [R(int) = 0.0243]. The structure was solved by direct methods SHELXS-86₁¹, and refined by full matrix least squares using SHELXS-97₁². SHELX operations were automated using ORTEX which was also used to obtain the drawings₁³. Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. After full matrix refinement the final R indices [I > 2σ(I)] were R₁ = 4.49% and wR₂ = 12.14% and R indices (all data) were R₁ = 5.01% and wR₂ = 12.77% > the maximum and minimum excursions in the final F₀ – Fc difference map were 0.233 and –0.337 eÅ⁻³. All calculations were performed on a Pentium PC.

References