Abstract
Isoxazol-5(2H)-ones undergo Michael addition to propiolate esters under mildly basic conditions to form N-alkenylisoxazolones, with small amounts of the isomeric C- or O-alkylated materials. The former lose carbon dioxide when subjected to flash vacuum pyrolysis or photolysis, and give pyrroles in ca 40% yields. Minor accompanying products arise from capture of the intermediate carbene by solvent, or from hydrogen atom abstraction.

Keywords: Pyrroles, N-alkenylisoxazol-5(2H)-ones, Michael addition, propiolate esters, flash vacuum pyrolysis, photolysis carbene

Introduction
In our study of the photochemical or thermal reactions of isoxazol-5(2H)-ones we have uncovered two new routes for the synthesis of pyrroles from these species. The first was an intermolecular reaction, in which the carbenoid intermediate obtained from the photolysis was reacted with an aromatic amine or an enamine (Scheme 1).
While this procedure holds some promise for the synthesis of indoles, the synthesis of pyrroles by this procedure is somewhat limited. In a more recent communication we reported the photolysis and flash vacuum pyrolysis of two $N$-alkenylisoxazolones (Scheme 2). It appeared that photochemical reactions led to the desired pyrrole in variable yields, but that flash vacuum pyrolysis (FVP) led to a number of rearrangements. Since $N$-alkenylobenzotriazoles have been utilised by a number of workers to synthesise indoles by reactions that are formally analogous to these, in the present study we seek to extend and define the limitations of our preliminary investigation.

Scheme 2

Results and Discussion

The accessibility of the required $N$-alkenylisoxazolone intermediates appeared the major limitation. The synthesis of the analogous $N$-alkenylobenzotriazoles has created considerable interest, so we examined a number of these successful approaches, but they appear to be non-transferable to the isoxazolones. Thus Rees and Storr showed that $N$-chlorobenzotriazoles could be added to alkenes, and base catalysed elimination then formed the $N$-alkenyl compound (Scheme 3).

Scheme 3
Because of the sensitivity of isoxazolones towards base,\textsuperscript{10} this procedure would always be of limited application. In the event, we have found that reaction of several isoxazolones, such as 1, with NBS or t-butyl hypochlorite occurs at carbon rather than nitrogen, the assignment being based primarily on the $^{13}$C nmr resonance of C-4 in the product 2 at 49.3 ppm (Scheme 4), confirming the earlier report of De Sarlo\textsuperscript{11} with another isoxazolone. In spite of the formation of the 4-bromo or chloro compounds, the products should be good electrophiles, and it appeared possible that addition to alkenes could still give the desired compounds through the intermediate bromonium ion 3, but in the event addition of 2 and styrene gave the C-4 adduct, 4.

\textbf{Scheme 4}

An alternative approach was to react the salt of the isoxazolone with a vinyl triflate, readily prepared from the corresponding ketone. However, we have been unable to observe any such substitution; presumably the isoxazolone is insufficiently nucleophilic.\textsuperscript{12}

In view of the above failure to obtain the $N$-alkenylisoxazolones, we have investigated in further detail the procedure we had used previously,\textsuperscript{3} the addition of isoxazolones to propiolic esters. The necessity for base catalysis creates difficulties with 3-unsubstituted isoxazolones, as we had noted previously\textsuperscript{13} in the reaction of 4-phenylisoxazolone with ethyl propiolate: while reaction in the presence of triethylamine at room temperature in benzene gave the $N$-alkenyl product, in ethanol at 80°C the $N$-alkylated isoxazolone rearranged to the malonamide (Scheme 5).

\textbf{Scheme 5}

The reaction of the 4-ethoxycarbonylisoxazolone 5 with ethyl propiolate in benzene in the presence of triethylamine at room temperature gave a solid whose structure was shown to be the salt 6a. Thus, although the product showed the desired vinyl doublets at $\delta$ 6.31 and 7.20 ppm, the infrared absorption had dropped from 1760 cm$^{-1}$ to 1718 cm$^{-1}$, consistent with the anionic charge. Addition of dilute HCl to the salt allowed recovery of the isoxazolone 5. When the salt was
heated, either under FVP conditions at 540°C, or simply sublimed at 150 °C, the isoxazolone 5 was recovered, together with the Hofmann elimination product ethyl 3-diethylaminopropenoate 7a (Scheme 6). McCulloch and McInnes have reported that triethylamine reacts with ethyl propiolate to give the betaine 8, isolated only in low yield. This suggested to us that reaction of triethylamine with ethyl propiolate to form the acetylide is rapid, and the isoxazolone 5 functions mainly to allow rearrangement to the zwitterion 9 which is rapidly protonated. Indeed, nmr observation showed that triethylamine and ethyl propiolate react essentially instantly in CDCl₃ at 28 °C, presumably to form the acetylide, but the formation of 6a requires 2-3 h for completion.

Scheme 6

Since the reaction of 5 and ethyl propiolate did not occur under neutral or acidic conditions, we examined the reaction in the presence of more hindered bases. Isoxazolone 5 was recovered unchanged after exposure to ethyl propiolate at 25 °C in the presence of diisopropylethylamine, but the formation of ethyl 3-diisopropylaminopropenoate 7b suggested the formation of the betaine analogous to 6a had occurred, followed by rapid Hofmann elimination. In the presence of pyridine reaction was slow, and at 80 °C for 3 h the formation of a 1:2 mixture of the desired N-alkenyl product 10 and the 4-alkenyl product 11 was only 50% complete: the remainder was the pyridine salt of 5. The major, C-alkylated product was a mixture of (Z) and (E) isomers, with the (Z) diastereomer predominating. Reaction at room temperature did not proceed with either 1 or 5, yielding only the respective pyridine salt of the isoxazolone.

Reaction of 3-substituted isoxazolones 12a-12e with propiolate esters was less complicated, but traces of O-alkylated material were formed in most cases, but were readily separable by chromatography, which allowed the recovery of unreacted isoxazolone. Yields of N- and O-alkylated material, after chromatography, are shown in Table 1; yields of crude product were usually of the order of 75%.
Table 1. Products from the reaction of isoxazolones (12) with ethyl propiolate

<table>
<thead>
<tr>
<th>Isoxazolones</th>
<th>Propiolate</th>
<th>N-alkylation</th>
<th>O-alkylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>C₆H₅</td>
<td>H</td>
<td>28</td>
</tr>
<tr>
<td>12b</td>
<td>4-Cl C₆H₄</td>
<td>H</td>
<td>26</td>
</tr>
<tr>
<td>12c</td>
<td>4-OMe C₆H₄</td>
<td>H</td>
<td>43</td>
</tr>
<tr>
<td>12d</td>
<td>2-naphthyl</td>
<td>H</td>
<td>29</td>
</tr>
<tr>
<td>12e</td>
<td>CH₃</td>
<td>H</td>
<td>39</td>
</tr>
<tr>
<td>12e</td>
<td>CH₃</td>
<td>CH₃</td>
<td>41</td>
</tr>
<tr>
<td>12e</td>
<td>CH₃</td>
<td>C₆H₅</td>
<td>71</td>
</tr>
</tbody>
</table>

The isoxazolones 13 were photolysed through pyrex in acetone, or subjected to FVP, yielding the desired pyrrole 15 as the major product, sometimes accompanied by the isomeric pyrrole 16, presumably formed by prior isomerisation of the carbene intermediate (Scheme 7). Isolated yields, after chromatography, are shown in Table 2.

Table 2. Pyrroles from isoxazolones

<table>
<thead>
<tr>
<th>Isoxazolone</th>
<th>% Yield of Pyrrole</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>hv FVP</td>
</tr>
<tr>
<td>13a</td>
<td>61 0</td>
</tr>
<tr>
<td>13b</td>
<td>21 0</td>
</tr>
<tr>
<td>13c</td>
<td>23 12</td>
</tr>
<tr>
<td>13d</td>
<td>24 -</td>
</tr>
<tr>
<td>13e</td>
<td>- 66</td>
</tr>
<tr>
<td>13f</td>
<td>- 93</td>
</tr>
<tr>
<td>13g</td>
<td>- 19</td>
</tr>
</tbody>
</table>
The pyrroles 15 and 16 were readily distinguishable by nmr spectroscopy, and were generally accompanied by more minor products that were informative of the reaction pathways that are open to this system. Inspection of Table 2 shows that the rearranged pyrroles 16 are formed predominantly with the isoxazolones 13c and 13d, suggesting that electron rich groups promote the carbene rearrangement by stabilising the intermediate 1H-azirine (Scheme 8).

Scheme 8

The products from the FVP of the 2-naphthylisoxazolone 13d were investigated in more detail, but are typical in that isolated products total ca 70-75%. Photolysis of 13d gave a mixture of five products, as assessed by gc/ms. The pyrroles 15d and 16d were isolated by chromatography, and the structures established by comparison of their spectral data. A third product was characterised as 2-acetylnaphthalene 17 (10%), and another as an acetone addition compound, whose structure remains uncertain (19%). The minor component (1%) was the 4-(2-naphthyl)oxazole 18. This compound is derived from the nitronoketene isomer of the isoxazolone, in an analogous process to that described previously.³ Three of the other compounds are derived from the imidoylcarbene, the 2-acetylnaphthalene arising from the triplet state by hydrogen atom abstraction from the acetone solvent, followed by hydrolysis during chromatographic purification (Scheme 9). The acetone adduct obtained from 13d is not of the same type as isolated from other compounds. For instance, photolysis of 19 gave the expected pyrrole 20 in only 15% yield, but this was accompanied by 70% of the acetone adduct 21. The sp³ bound methyl groups in 21 were non equivalent in the 1H and 13C nmr spectra, but the acetone adduct obtained from 13d is an adduct of the isoxazolone and acetone, having lost neither CO₂ nor CO, and with magnetically equivalent C-Me groups.

Finally, the FVP products from 13g included the pyrrole 15g in 19% isolated yield; the major product was isomeric with it, but appears to have a pyridone structure, and will be the subject of a separate investigation. We conclude that the above synthesis of pyrroles is limited by the lack of a general procedure to form the intermediate N-alkenyl isoxazolones. The conjugation of an ester with the double bond in these compounds clearly reduces the nucleophilicity of the double bond to the extent that what are usually minor reaction pathways of the imidoyl carbene now become significant.
Ar = 2-naphthyl

Scheme 9

Experimental Section

General Procedures. NMR spectra were recorded in CDCl₃ unless otherwise stated, using a Varian Mercury 200 Spectrometer operating at 200 MHz and 50 MHz for ¹H and ¹³C respectively or a Varian Gemini 300 Spectrometer operating at 300 MHz and 75.5 MHz. Infrared spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using fused sodium chloride cells as nujol mulls for solids and as films for liquids. Mass spectra and accurate mass determination were recorded on a Kratos MS25RF spectrometer. GC/MS analyses were performed on a Varian Saturn 4D GC/MS using a J & W DB5 5% phenyl methyl polysiloxane column (30m, 0.25mm ID, 0.25mm thickness). Centrifugal chromatography was performed using a Chromatotron (model 7924T) with silica gel 60 PF254. All column chromatography was performed using Reidel-de Haen Silica gel S. Merck silica gel 60 F254 aluminium backed sheets were used for analytical thin layer chromatography. All melting points are uncorrected. Photolyses were performed at 300nm using a low-pressure mercury lamp, filtered by using pyrex glassware.
Ethyl 4-bromo-3-methyl-5-oxo-2,5-dihydroisoxazole-4-carboxylate (2). Ethyl 3-methyl-5-oxo-2,5-dihydroisoxazole-4-carboxylate 1 (750 mg; 4.4 mmol) was stirred with a suspension of N-bromosuccinimide (780 mg; 4.4 mmol) in carbon tetrachloride (30 mL) for 40 min at rt. The succinimide was removed and the filtrate was washed with water, dried and evaporated to give the title compound as clear yellow oil (0.97 g; 88%). 1H NMR: δ: 4.34, q, J 6.5 Hz, 2H; 2.23, s, 3H; 1.31, t, J 6.6 Hz, 3H. 13C NMR: δ: 169.7, 162.6, 160.0, 65.3, 49.3, 13.7, 12.3. The compound did not give a molecular ion.

Ethyl 4-chloro-3-methyl-5-oxo-2,5-dihydroisoxazole-4-carboxylate. A solution of t-butyl hypochloride (190 mg; 1.8 mmol) in benzene (10 mL) was added dropwise over 10 minutes to a suspension of 1 (300 mg; 1.8 mmol) in benzene (10 mL) at 0°C. After 40 min the solution was evaporated to give the crude title compound (165 mg; 56%). 1H NMR: δ: 4.13, q, J 7Hz, 2H; 2.28, s, 3H; 1.17, t, J 7Hz, 3H. 13C NMR: δ: 168.7; 162.8; 161.9; 65.1; 59.5; 13.5; 11.5. The compound did not give a molecular ion.

Attempted synthesis of ethyl 4-(2-bromo-1-phenylethyl)-3-methyl-5-oxo-2,5-dihydroisoxazole-4-carboxylate (4). A mixture of isoxazolone 1 (300 mg), N-bromosuccinimide (312 mg) and styrene (187 mg) was stirred for 16 h in carbon tetrachloride or dichloromethane (15 mL). The mixture was filtered and the solvent evaporated to give oil, which contained ca 25% of the title compound as well as starting material. 1H NMR for 4: δ: 4.25, d, J = 7 Hz, 2H; 3.85, m, 1H; 3.62, dd, J 10 Hz, 3 Hz, 1H; 3.55, dd, J 10 Hz, 9 Hz, 1H; 2.20, s, 3H; 1.31, t, J 7Hz, 3H. 13C NMR: δ: 170.2; 160.1; 153.9; 129.5; 126.4; 65.3; 60.5; 47.4; 41.2; 14.4; 12.2. When reaction was extended to 4 d at rt, nmr analysis indicated that the reaction was still only 50% complete.

No reaction occurred with cyclohexene under similar conditions.

2-Ethoxycarbonylethenyltriethylammonium 4-ethoxycarbonylisoxazole-5-oxide (6a) (i) Triethylamine (370 mg; 3.66 mmol) was added to a stirred suspension of ethyl 5-oxo-2,5-dihydroisoxazole-4-carboxylate 5 (505 mg; 3.21 mmol) and ethyl propiolate (347 mg; 3.57 mmol) in benzene (15 mL). The solution was stirred for 16 h at room temperature after which time the solvent was evaporated leaving 6a as a white solid (1.12 g; 95%), mp. 128°C dec. 1H NMR: δ: 8.18, s, 1H; 7.20, d, J 9.6 Hz, 1H; 6.31, d, J 9.6 Hz, 1H; 4.25, q, J 7.2 Hz, 2H; 4.13, q, J 7.2Hz, 2H; 3.79, q, J 7.2 Hz, 6H; 1.37, t, J 7.2 Hz, 9H; 1.29, t, J 7.2 Hz, 6H. 13C NMR: δ: 176.7; 165.0; 162.8; 153.8; 145.3; 123.4; 80.2; 62.3; 58.1; 55.3; 14.8; 13.9; 8.0. vmax: 1718, 1636 cm⁻¹.

An analogous product 6b was obtained in >90% yield when 1 was reacted as above. 1H NMR: δ: 7.18, d, J 14 Hz, 1H; 6.36, d, J 14 Hz, 1H; 4.19, q, J 7.2 Hz, 2H; 4.10, q, J 7.2Hz, 2H; 4.10, q, J 7.2Hz, 2H; 3.72, q, J 7.2 Hz, 6H; 2.18, s, 3H; 1.2-1.35, m, 15H. 13C NMR: δ: 165.0; 162.5; 145.3; 133.5; 123.4; 118.6; 98.7; 62.4; 58.0; 55.4; 14.8; 14.5; 13.9; 8.1.

(ii) Isoxazolone 5 (51 mg; 0.32 mmol), ethyl propiolate (84 mg; 0.86 mmol) and triethylamine (61 mg; 0.60 mmol) were dissolved in an NMR tube in deuterated chloroform and analysed at 15 min intervals over 3 h. This revealed that the reaction of the triethylamine with the ethyl propiolate was almost instantaneous, with the isoxazolone forming its respective anion much more slowly.

Pyrolysis of 6a. (i) Compound 6a (220 mg; 0.62 mmol) was sublimed at 150°C and passed
through the pyrolysis column at 540 °C. GC/MS analysis revealed the presence of four products. The most volatile was confirmed to be ethyl cyanoacetate (20%) by direct comparison. The second product (10%) is believed to be ethyl 3-ethylaminopropenoate from examination of its mass spectrum. The third product was compound 7a, (50%), and the fourth (10%) is unidentified.

(ii) Sublimation of 6a at 150 °C/0.03 mm gave an oil, the major component of which was identified as ethyl (E)-3-diethylaminopropenoate 7a.

(iii) Compound 6a (475 mg; 1.3 mmol) was dissolved in xylene and the solution refluxed for 30 min. The solvent was evaporated to give a clean sample of ethyl (E)-3-diethylaminopropenoate 7a. (Found: M⁺, 171.1264. C₉H₁₇NO₂ requires M⁺, 171.1259). ¹H NMR δ: 7.42, d, J 12 Hz, 1H; 4.55, d, J 12 Hz, 1H; 4.11, q, J 7Hz, 2H; 3.16, q, J 7Hz, 4H; 1.24, t, J 7 Hz, 3H; 1.13, t, J 7 Hz, 6H. ¹³C NMR δ: 170.0; 150.8; 83.2; 63.6; 58.7; 14.6; 13.9. Mass spectrum m/z: 171 (M+, 45), 156 (15), 142 (81), 126 (100), 98 (54), 86 (66).

**Ethyl (E)-3-diisopropylaminopropenoate (7b).** Di-isopropylethylamine (250 mg; 1.9 mmol) was added to a stirred suspension of ethyl 5-oxo-2,5-dihydroisoxazole-4-carboxylate 5 (300 mg; 1.9 mmol) and ethyl propiolate (200 mg; 2.0 mmol) in ethanol (15 mL). The solution was refluxed for 3 h and the solvent was evaporated. The major product was ethyl (E)-3-diisopropylaminopropenoate 7b. (Found: M⁺, 199.1580. C₁₁H₂₁NO₂ requires M⁺, 199.1572). ¹H NMR δ : 7.50, d, J 10 Hz, 1H; 4.55, d, J 10 Hz, 1H; 4.13, q, J 6 Hz, 2H; 3.70, sep, J 6.5 Hz, 2H; 1.41, d, J 6.5 Hz, 6H; 1.25, t, J 6 Hz, 3H. ¹³C NMR δ: 164.7; 153.5; 83.2; 63.6; 58.4; 18.7; 14.6.

**Attempted synthesis of ethyl 2-(2-ethoxycarbonylethenyl)-5-oxo-2,5-dihydroisoxazole-4-carboxylate (10).** Pyridine (5 drops) was added to a stirred suspension of 5 (300 mg; 1.9 mmol) and ethyl propiolate (200 mg; 2.0 mmol) in ethanol (15 mL). The solution was refluxed for 3 h and the solvent was evaporated. The residue was taken up in ether (50 mL) and washed with 2M HCl (2 x 20 mL). The ethereal layer was evaporated. NMR analysis showed the product to consist of a mixture of 10 and 11 in the ratio of 2:1 (55%), ethyl cyanoacetate (15%), and the pyridine salt of 5 (30%). Diagnostic ¹H NMR 10, δ : (Z) isomer 6.46, d, J 10 Hz; 7.90, d, J 10 Hz); (E) isomer, 5.95, d, J 16 Hz; 7.60, d, J 16 Hz; Diagnostic ¹H NMR 11, δ : (Z) isomer 5.41, d, J 11 Hz; 6.76, d, J 11 Hz); (E) isomer 6.62, d, J 14 Hz; 7.05, d, J 14 Hz.

No product formation was observed in the absence of base in CH₂Cl₂ (16 h, 40 °C), or benzene with 2 equiv. CF₃CO₂H (6 h, 50 °C). In toluene (16 h, 110 °C), NMR analysis indicated the presence of (E)-10, (7%), and (Z)-11, (10%); the major product (80%) was ethyl cyanoacetate.

**Reaction of 3-(4-chlorophenyl)isoxazol-5(4H)-one with ethyl propiolate.** 3-(4-Chlorophenyl)isoxazol-5(4H)-one 15b (0.25 g, 1.3 mmol), ethyl propiolate (0.125 g, 1.3 mmol) and triethylamine (0.129 g, 1.3 mmol) were refluxed in dichloromethane (10 mL) for 6h. The solvent was evaporated and the residue was redissolved in ether (30 mL) and then washed with 1M HCl (2 x 20 mL). The organic layer was separated, dried (Na₂SO₄), filtered and evaporated to give clear yellow oil (0.262 g, 70%), which was purified by radial chromatography (10% ethyl acetate/light petroleum) to give three fractions. The first fraction contained 3-(4-chlorophenyl)-5-
(2-ethoxycarbonylethenyloxy)isoxazole 14b as a white solid (0.029 g, 8%), m.p. 78-80 °C (Found: M+, 293.0456. C\(\text{_{14}}\)H\(\text{_{12}}\)NO\(\text{_{4}}\)Cl requires M+, 293.0455). \(^1\)H NMR. δ 7.82, d, J 11.9 Hz, 1H; 7.69, d, J 8.4 Hz, 2H; 7.43, d, J 8.4 Hz, 2H; 5.90, d, J 12 Hz, 1H; 5.86, s, 1H; 4.24, q, J 7.1 Hz, 2H; 4.17, q, J 7.1 Hz, 2H; 1.31, t, J 7.1 Hz, 3H. 13C NMR δ 169.9, 165.7, 163.7, 153.9, 136.9, 129.5, 128.0, 127.4, 107.4, 80.1, 61.0. \(\nu\) max 1709, 1622, 1464 cm\(^{-1}\). Mass spectrum (m/z) 293 (M+, 2.5%), 224 (22), 196 (20), 179 (84), 150.5 (72), 139 (100), 123 (34), 111 (28), 75 (32), 50 (25).

The second fraction contained ethyl (E)-3-(3-(4-chlorophenyl)-5-oxo-2,5-dihydroisoxazol-2-yl)propenoate 13b as a pale yellow powder (0.088 g, 23%), mp. 108-110 °C. (Found: M+, 293.0455. C\(\text{_{14}}\)H\(\text{_{12}}\)NO\(\text{_{4}}\)Cl requires M+, 293.0455). \(^1\)H NMR δ 7.41-7.58, m, 5H; 5.88, d, J = 13.4 Hz, 1H; 5.49, s, 1H; 4.17, q, J = 7.0 Hz, 2H; 1.26, t, J = 7.0 Hz, 3H. 13C NMR δ 166.7, 166.5, 159.6, 139.0, 132.9, 130.4, 129.9, 123.8, 102.9, 91.8, 60.9. \(\nu\) max 1774, 1709, 1635, 1608, 1579, 1559, 1487 cm\(^{-1}\). Mass spectrum (m/z) 293 (M+, 70%), 248 (60), 221 (27), 220 (22), 180 (62), 178 (100), 150 (87), 136 (97), 101 (38), 84 (54), 75 (57), 44 (87). The third fraction contained ethyl (Z)-3-(3-(4-chlorophenyl)-5-oxo-2,5-dihydroisoxazol-2-yl)propenoate 13b as a pale yellow solid (0.012 g, 3%), mp. 120-122 °C (Found: M+, 293.0454. C\(\text{_{14}}\)H\(\text{_{12}}\)NO\(\text{_{4}}\)Cl requires M+, 293.0455). \(^1\)H NMR δ 7.4-7.56, m, 4H; 6.43, d, J = 9.7 Hz, 1H; 5.47, s, 1H; 5.35, d, J = 9.7 Hz, 1H; 4.34, q, J = 7.1 Hz, 2H; 1.35, t, J = 7.1 Hz, 3H. 13C NMR δ 167.4, 164.3, 160.7, 138.6, 129.9, 129.7, 126.8, 124.4, 105.8, 90.6, 61.2, 14.0. \(\nu\) max 1751, 1732, 1647, 1487 cm\(^{-1}\). Mass spectrum (m/z) 293 (M+, 25%), 248 (29), 221 (14), 203 (10), 163 (16), 136 (61), 101 (26), 84 (44), 44 (100).

**Photolysis of 13b.** The (E) isomer 13b (0.08 g, 0.27mmol) was photolysed through pyrex at 300 nm in anhydrous acetone (150 mL) under N\(_2\) at room temperature for 3h. The solvent was evaporated and the residue was purified by radial chromatography (10% ethyl acetate/light petroleum) to give two main fractions.

The first fraction contained 4-chloroacetophenone (0.005 g, 10%), isolated as a colourless oil, the structure of which was confirmed by comparison with an authentic sample. \(^1\)H NMR δ 7.89, d, J = 8.3 Hz, 2H; 7.43, d, J = 8.3 Hz, 2H; 2.61, s, 3H. 13C NMR δ 197.3, 137.2, 131.22, 129.3, 128.7, 27.4.

The second fraction contained ethyl 5-(4-chlorophenyl)pyrrole-3-carboxylate 15b, isolated as a white powder (0.014g, 21%), m.p. 130-132 °C (Found: M+, 249.0557. C\(\text{_{13}}\)H\(\text{_{12}}\)NO\(\text{_{2}}\)Cl requires M+, 249.0557). \(^1\)H NMR δ 9.49, bs, 1H, NH; 7.51, d, J = 8.8 Hz, 2H; 7.37, d, J = 8.8 Hz, 2H; 6.95, dd, J = 2.4 , 4.0 Hz, 1H; 6.51, dd, J = 2.4 , 4.0 Hz, 1H; 4.34, q, J = 7.1 Hz, 2H; 1.37, t, J = 7.1 Hz, 3H. 13C NMR δ 161.3, 135.5, 133.5, 129.9, 129.2, 125.9, 123.8, 116.7, 108.3, 60.5, 14.5. \(\nu\) max 1686 cm\(^{-1}\). Mass spectrum (m/z) 249 (M+, 72), 204 (100), 175 (19), 149 (23), 140 (46), 111 (7), 75 (8), 43 (14).

**Reaction of 3-(4-methoxyphenyl)isoxazol-5(4H)-one with ethyl propiolate.** 3-(4-Methoxyphenyl)isoxazol-5(4H)-one\(^{15}\) 12c (0.26 g, 1.36 mmol), ethyl propiolate (0.133g, 1.36 mmol) and triethylamine (0.137 g, 1.36 mmol) were reacted as above. The product (0.303 g) was purified by radial chromatography (10% ethyl acetate/light petroleum), to give three main fractions.
The first fraction contained 5-(2-ethoxycarbonylenethyloxy) 3-(4-methoxyphenyl)isoxazole 14c as a clear oil (0.03 g, 8%). (Found: M⁺, 289.0952. C₁₅H₁₅NO₅ requires M⁺, 289.0950). \( ^1H \) NMR δ 8.06, d, \( J = 12.6 \) Hz, 1H; 7.66, d, \( J = 8.6 \) Hz, 2H; 7.26, s, 1H; 6.91, d, \( J = 8.6 \) Hz, 2H; 5.66, d, \( J = 12.6 \) Hz, 1H; 4.19, q, \( J = 7.1 \) Hz, 2H; 3.84, s, 3H; 1.29, t, \( J = 7.1 \) Hz, 3H. \( ^13C \) NMR δ 169.3, 165.4, 162.8, 155.3, 134.2, 129.7, 114.3, 113.5, 112.9, 84.4, 61.3, 56.1, 14.4.

The second fraction contained ethyl (E)-3-\{3-(4-methoxyphenyl)-5-oxo-2,5-dihydroisoxazol-2-yl\}propenoate 13c as a fine yellow powder (0.139 g, 35%), m.p. 122°C. (Found: M⁺, 289.0954. C₁₅H₁₅NO₅ requires M⁺, 289.0950). \( ^1H \) NMR δ 7.58, d, \( J = 13.2 \) Hz, 1H; 7.42, d, \( J = 8.6 \) Hz, 2H; 7.04, d, \( J = 8.6 \) Hz, 2H; 5.86, d, \( J = 13.2 \) Hz, 1H; 5.42, s, 1H; 4.16, q, \( J = 7.1 \) Hz, 2H; 3.88, s, 3H; 1.25, t, \( J = 7.1 \) Hz, 3H. \( ^13C \) NMR δ 166.5, 162.6, 160.6, 133.4, 130.1, 129.9, 117.1, 115.1, 101.9, 90.4, 60.5, 55.5, 14.1. υ max 1770, 1709, 1633, 1611, 1507, 1442 cm⁻¹. Mass spectrum (m/z) 289 (M⁺, 15%), 234 (13), 204 (6), 159 (9), 151 (31), 135 (100), 92 (14), 84 (50).

The third fraction contained the (Z) isomer of 13c, isolated as white needles (0.032 g, 8%), m.p. 53-54 °C. (Found: M⁺, 289.0952. C₁₅H₁₅NO₅ requires M⁺, 289.0950). \( ^1H \) NMR δ 7.81, d, \( J = 12.1 \) Hz, 1H; 7.68, d, \( J = 8.6 \) Hz, 2H; 6.96, d, \( J = 8.6 \) Hz, 2H; 5.88, d, \( J = 12.1 \) Hz, 1H; 5.83, s, 1H; 4.23, q, \( J = 7.1 \) Hz, 2H; 3.84, s, 3H; 1.31, t, \( J = 7.1 \) Hz, 3H. \( ^13C \) NMR δ 169.3, 164.1, 161.3, 153.6, 127.9, 127.8, 114.3, 114.1, 114.3, 106.8, 79.6, 60.7, 55.3, 14.2. υ max 1750, 1714, 1666, 1605, 1574, 1531 cm⁻¹. Mass spectrum (m/z) 289 (M⁺, 2.5%), 150 (19), 135 (100), 92 (14), 77 (21), 43 (7).

**Photolysis of 13c.** The (E) isomer of 13c (0.103 g, 0.36 mmol) was photolysed through pyrex at 300 nm in anhydrous acetone (150 mL) under N₂ at room temperature for 3h. Purification by radial chromatography (10% ethyl acetate/light petroleum) gave three fractions.

The first fraction contained 4-methoxyacetophenone as a pale yellow oil (0.016 g, 30%), the identity of which was confirmed by direct comparison with an authentic sample.

The second fraction contained ethyl 5-(4-methoxyphenyl)pyrrole-3-carboxylate 15c as a white solid (0.02 g, 23%), mp. 123 °C. (Found: M⁺, 245.1051. C₁₄H₁₅NO₃ requires M⁺, 245.1052). \( ^1H \) NMR δ 9.45, bs, 1H, NH; 7.50, d, \( J = 8.9 \) Hz, 2H; 6.96, d, \( J = 8.9 \) Hz, 2H; 6.95, dd, \( J = 2.7 \), 3.9 Hz, 1H; 6.43, dd, \( J = 2.7 \), 3.9 Hz, 1H; 4.33, q, \( J = 7.1 \) Hz, 2H; 3.83, s, 3H; 1.37, t, \( J = 7.1 \) Hz, 3H. \( ^13C \) NMR δ 161.3, 136.9, 131.8, 126.1, 114.3, 114.4, 106.8, 79.6, 60.7, 55.3, 14.2. υ max 1770, 1709, 1633, 1611, 1507, 1442 cm⁻¹. Mass spectrum (m/z) 245 (M⁺, 50), 199 (66), 171 (22), 145 (17), 135 (100), 128 (12), 92 (13), 77 (24), 43 (9).

The third fraction contained ethyl 4-(4-methoxyphenyl)pyrrole-3-carboxylate 16c which was isolated as a pale yellow solid (0.016 g, 30%), mp. 123 °C. (Found: M⁺, 245.1051. C₁₄H₁₅NO₃ requires M⁺, 245.1052). \( ^1H \) NMR δ 8.77, bs, 1H, NH; 7.44, dd, \( J = 1.6 \), 3.2 Hz, 1H; 7.40, d, \( J = 8.9 \) Hz, 2H; 6.92, d, \( J = 8.9 \) Hz, 2H; 6.79, dd, \( J = 1.6 \), 3.2 Hz, 1H; 4.3, q, \( J = 7.1 \) Hz, 2H; 3.83, s, 3H; 1.35, t, \( J = 7.1 \) Hz, 3H. \( ^13C \) NMR δ 165.2, 130.1, 125.8, 123.7, 114.7, 113.8, 109.9, 105.8, 82.1, 59.9, 55.6, 14.7. υ max 1711, 1566 cm⁻¹. Mass spectrum (m/z) 245 (M⁺, 100%), 230 (23), 217 (29), 202 (42), 173 (15), 145 (12), 135 (40), 100 (9), 87 (13).

**3-(2-Naphthyl)isoxazol-5(4H)-one (12d).** Ethyl naphthoylacetate 16 (0.5 g, 2.1 mmol) and hydroxylamine hydrochloride (0.2 g, 6.3 mmol) were heated in water (5 mL) at 100 °C for 5min.
Ethanol (8 mL) was added until homogeneity was achieved, and heating was then continued for 30 min. The mixture was then chilled and the product was collected and washed with cold ethanol, giving pale pink needles of the title compound (0.33 g, 76%), mp. 148-151 °C. (Found: M+, 211.0634. C13H9NO2 requires M+, 211.0633). 1H NMR δ 7.87-7.94, m, 5H; 7.54-7.64, m, 2H; 3.91, s, 2H. 13C NMR δ 174.7, 163.0, 134.9, 132.7, 129.2, 128.7, 128.2, 128.0, 127.9, 127.3, 125.1, 121.9, 33.9. νmax 1798, 1560, 1176 cm⁻¹. Mass spectrum (m/z) 211 (M+, 100%), 199 (4), 185 (10), 169 (14), 153 (80), 143 (25), 127 (30), 111 (11), 97 (18), 83 (23), 73 (32), 57 (40), 43 (45).

**Reaction of 3-(2-Naphthyl)isoxazol-5(4H)-one 12d with ethyl propiolate**

3-(2-Naphthyl)isoxazol-5(4H)-one (0.33 g, 1.56 mmol), ethyl propiolate (0.153 g, 1.56 mmol) and triethylamine (0.16 g, 1.56 mmol) were reacted as above. The product, an orange oil (0.422 g), was purified by radial chromatography (10% ethyl acetate/light petroleum) to give three fractions.

The first fraction contained (E)-5-(2-ethoxycarbonylethenyloxy)-3-(2-naphthyl)isoxazole 14d and its (Z) isomer, as a colourless oil (0.05 g, 9%). (Found: M+, 309.1006. C18H15NO4 requires M+, 309.1001). 1H NMR δ 8.17, s, 1H; 7.83-7.91, m, 4H; 7.51-7.57, m, 3H; 6.00, s, 1H; 5.91, d, J = 12.1 Hz, 1H; 4.25, q, J = 7.1 Hz, 2H; 1.33, t, J = 7.1 Hz, 3H. 13C NMR δ 169.6, 165.5, 164.4, 153.8, 135.8, 134.2, 133.0, 128.8, 128.5, 127.8, 127.2, 126.7, 126.6, 107.0, 80.0, 60.8, 14.2. νmax 1722, 1684, 1655, 1596, 1558, 1460 cm⁻¹. Mass spectrum (m/z) 309 (M+, 22%), 276 (4), 242 (21), 194 (15), 183 (3), 166 (11), 155 (100), 139 (8), 127 (54), 115 (4), 77 (6). The second fraction contained ethyl (E)-3-{3-(2-naphthyl)-5-oxo-2,5-dihydroisoxazol-2-yl}propenoate 13d which was obtained as a pale yellow solid (0.1 g, 21%), mp. 150-152 °C. (Found: M+, 309.0997. C18H15NO4 requires M+, 309.1001). 1H NMR δ 7.99-8.02, m, 2H; 7.91-7.95, m, 2; 7.61-7.65, m, 3H; 7.48-7.51, m, 1H; 5.91, d, J = 13.5 Hz, 1H; 5.60, s, 1H; 4.15, q, J = 7.1 Hz, 2H; 1.23, t, J = 7.1 Hz, 3H. 13C NMR δ 166.8, 166.3, 160.8, 134.5, 133.3, 132.7, 129.8, 129.1, 128.7, 128.6, 127.9, 127.7, 124.0, 122.2, 102.3, 91.5, 60.5, 14.2. νmax 1771, 1703, 1636, 1568, 1277 1182 cm⁻¹. Mass spectrum (m/z) 309 (M+, 100%), 281 (20), 264 (43), 236 (62), 219 (66), 192 (71), 179 (40), 165 (60), 152 (100), 139 (8), 127 (48), 115 (8), 69 (16). The third fraction contained ethyl (Z)-3-{3-(2-naphthyl)-5-oxo-2,5-dihydroisoxazol-2-yl}propenoate which was obtained as a yellow oil (0.04 g, 8%). (Found: M+, 309.1006. C18H15NO4 requires M+, 309.1001). 1H NMR δ 8.00-8.04, m, 2H; 7.91-7.96, m, 2H; 7.61-7.65, m, 2H; 7.50-7.55, m, 1H; 6.53, d, J = 9.5 Hz, 1H; 5.55, s, 1H; 5.32, d, J = 9.5 Hz, 1H; 4.29, q, J = 7.1 Hz, 2H; 1.35, t, J = 7.1 Hz, 3H. 13C NMR δ 167.0, 164.2, 162.0, 134.5, 133.2, 132.7, 129.8, 129.5, 129.1, 128.6, 128.5, 127.9, 127.6, 124.3, 105.0, 90.5, 61.1, 14.0. νmax 1750, 1732, 1655, 1560 cm⁻¹. Mass spectrum (m/z) 309 (M+, 96%), 293 (13), 281 (19), 264 (50), 247 (20), 236 (68), 219 (66), 208 (63), 192 (70), 179 (39), 165 (52), 152 (100), 139 (26), 127 (50), 115 (8), 96 (5), 69 (16), 55 (6). **Photolysis of 13d**

The (E) isomer (0.1 g, 0.32 mmol) was photolysed through pyrex at 300 nm in anhydrous
acetone (150 mL) for 3 h as above. Radial chromatography (10% ethyl acetate/light petroleum) gave four fractions.

The first fraction contained 2-acetylnaphthalene 17 (0.01 g, 18%), m.p. 53 °C (lit.17 mp. 54 °C), and had spectral data identical to that found in the literature.17 1H NMR δ 8.47, s, 1H; 7.87-8.06, m, 4H; 7.53-7.64, m, 2H; 2.73, s, 3H. 13C NMR δ 197.8, 135.5, 134.4, 132.4, 130.0, 129.4, 128.34 128.3, 127.7, 126.6, 123.8, 26.6. υmax 1682 cm\(^{-1}\). Mass spectrum (m/z) 170 (M\(^{+}\), 50%), 155 (100), 127 (59), 115 (5), 101 (6), 87 (4), 77 (7), 63 (8), 50 (5), 43 (17).

The second fraction contained ethyl 5-(2-naphthyl)pyrrole-3-carboxylate 15d as a white solid (0.02 g, 24%), mp. 120-122 °C. (Found: M\(^{+}\), 265.1103. C\(_{17}\)H\(_{15}\)NO\(_{2}\) requires M\(^{+}\), 265.1103). 1H NMR δ 9.55, bs, 1H, NH; 8.00, s, 1H; 7.82-7.89, m, 3H; 7.69-7.72, m, 1H; 7.45-7.54, m, 2H; 7.01, dd, J = 2.5, 3.9 Hz, 1H; 6.67, dd, J = 2.5, 3.9 Hz, 1H; 4.36, q, J = 7.0 Hz, 2H; 1.38, t, J = 7.0 Hz, 3H. 13C NMR δ 161.3, 136.6, 133.5, 132.7, 128.8, 128.7, 127.0, 126.1, 123.6, 123.1, 123.0, 116.8, 108.4, 60.5, 14.5. υmax 3324, 1690 cm\(^{-1}\). Mass spectrum (m/z) 265 (M\(^{+}\), 60%), 219 (100), 191 (50), 165 (29), 155 (9), 127 (5), 109 (3), 95 (8), 82 (9).

The third fraction (0.022 g) contained a mixture of the oxazole 18 and an unidentified acetone addition product.

Oxazole 18: 1H NMR δ 8.08, s, 1H; 7.81-7.91, m, 4H; 7.71-7.75, m, 1H; 7.48-7.56, m, 2H; 4.33, q, J = 7.1 Hz, 2H; 3.78, s, 2H; 1.36, t, J = 7.1 Hz, 3H. Mass spectrum (m/z) 281 (M\(^{+}\), 3%), 262 (5), 196 (100), 167 (20), 127 (24).

Unidentified adduct: 1H n.m.r δ 10.18, bd, J = 12.36 Hz, 1H; 7.5-7.9, m, 7H; 6.58, dd, J = 8.4, 12.4 Hz, 1H; 6.28, d, J = 2.9 Hz, 1H; 4.77, d, J = 8.4 Hz, 1H; 4.39, q, J = 7.14 Hz, 2H; 1.73, s, 6H; 1.4, t, J = 7.14 Hz, 3H. Mass spectrum (m/z) 323(M+(CH\(_{3}\))\(_{2}\)CO\(^{+}\), 93%), 277 (100), 249 (29), 190 (28), 163 (21).

The fourth fraction contained ethyl 4-(2-naphthyl)pyrrole-3-carboxylate 16d as a pale yellow oil (0.015 g, 17%). (Found: M\(^{+}\), 265.1097. C\(_{17}\)H\(_{15}\)NO\(_{2}\) requires M\(^{+}\), 265.1103). 1H NMR δ 9.06, bs, 1H, NH; 7.98-7.99, m, 1H; 7.71-7.75, m, 1H; 7.43-7.50, m, 2H; 7.04, dd, J = 1.5, 3 Hz, 1H; 7.43-7.50, m, 2H; 7.04, dd, J = 1.5, 3 Hz, 1H; 7.53, dd, J = 1.5, 3 Hz, 1H; 7.53, dd, J = 1.5, 3 Hz, 1H; 4.33, q, J = 7.1 Hz, 2H; 1.26, t, J = 7.14 Hz, 3H. Mass spectrum (m/z) 265 (M\(^{+}\), 100%), 252 (12), 237 (28), 220 (64), 193 (32), 180 (3), 165 (30), 155 (24), 139 (4), 127 (13), 110 (28), 95 (5), 82 (16), 44 (49).

**Reaction of 3-methylisoxazol-5(4H)-one with ethyl propiolate**

3-Methylisoxazol-5(4H)-one 12e (0.8 g, 8 mmol), ethyl propiolate (0.8 g, 8 mmol) and triethylamine (0.8 g, 8 mmol) were refluxed in dichloromethane (15 mL) for 30 min. Workup as above gave a pale orange solid (0.853 g), which was purified by radial chromatography (10% ethyl acetate/light petroleum), to give two main fractions.

The first fraction contained 5-(2-ethoxycarbonylenethyloxy)-3-methylisoxazole 14e as a colourless oil (0.07 g, 4%). (Found: M\(^{+}\), 197.0687. C\(_{9}\)H\(_{11}\)NO\(_{4}\) requires M\(^{+}\), 197.0688). 1H NMR δ 7.75, d, J = 12 Hz, 1H; 5.82, d, J = 12 Hz, 1H; 5.41, s, 1H; 4.13, q, J = 7.1 Hz, 2H; 2.23, s, 3H; 1.26, t, J = 7.1 Hz, 3H. 13C NMR δ 169.0, 165.5, 162.5, 153.8, 106.6, 82.2, 60.6, 14.1, 12.3. υmax
1716, 1659, 1626, 1608, 1498 cm⁻¹. Mass spectrum (m/z) 197 (M⁺, 22%), 169 (13), 152 (26), 128 (19), 112 (4), 99 (42), 82 (100), 71 (45), 54 (72), 42 (45).

The second fraction contained ethyl (E)-3-(3-methyl-5-oxo-2,5-dihydroisoxazol-2-yl) propenoate 13e which was obtained as a pale yellow solid (0.625 g, 39%), mp. 87-90 °C. (Found: M⁺, 197.0687. C9H11NO4 requires M⁺, 197.0688). ¹H NMR δ 7.49, d, J = 13.2 Hz, 1H; 5.72, d, J = 13.2 Hz, 1H; 5.19, q, J = 0.82 Hz, 1H; 4.16, q, J = 7.1 Hz, 2H; 2.31, d, J = 0.82 Hz, 3H; 1.24, t, J = 7.1 Hz, 3H. ¹³C NMR δ 166.7, 166.4, 156.3, 130.2, 100.6, 91.0, 60.4, 14.1, 11.5.

υmax 1759, 1698 cm⁻¹. Mass spectrum (m/z) 197 (M⁺, 22%), 169 (13), 152 (100), 136 (8), 125 (34), 113 (14), 99 (7), 85 (56), 67 (24), 54 (13), 43 (16).

Flash vacuum pyrolysis of ethyl (E)-3-(3-methyl-5-oxo-2,5-dihydroisoxazol-2-yl)propenoate (13e)

Pyrolysis (450 °C, 150 °C, 0.1 mmHg) of 13e (0.05 g, 0.25 mmol) gave pale brown oil (0.031 g), which was purified by radial chromatography (10% ethyl acetate/light petroleum) to give ethyl 5-methylpyrole-3-carboxylate 15e as a white powder (0.026 g, 66%), mp. 70 °C (lit. 18 70-71 °C). ¹H NMR δ 8.32, bs, 1H, NH; 7.28, dd, J = 1.6, 2.8 Hz, 1H; 6.30, bs, 1H; 4.26, q, J = 7.1 Hz, 2H; 2.26, s, 3H; 1.35, t, J = 7.1 Hz, 3H. ¹³C NMR δ 166.1, 128.9, 122.3, 116.2, 107.2, 61.7, 14.3, 12.6. υmax 1676, 1645, 1560, 1487 cm⁻¹.

Reaction of 3-methylisoxazol-5(4H)-one with ethyl but-2-yanoate

3-Methylisoxazol-5(4H)-one (1.0 g, 10 mmol), ethyl 2- butynoate (1.13 g, 10 mmol) and triethylamine (1.0 g, 10 mmol) were refluxed in ethanol (15mL) at for 16 h. The solvent was evaporated and the residue was redissolved in diethyl ether (30 mL) and washed with 1M HCl (2 x 20 mL). The organic layer was separated, dried (Na₂SO₄), filtered and evaporated to give an orange oil (1.29 g), which was purified by radial chromatography (20% ethyl acetate/light petroleum), to give two fractions.

The first fraction contained 5-(2-ethoxy carbonyl-1-methylethenyloxy)-3-methylisoxazole 14f as yellow oil (0.102 g, 5%), (Found: M⁺, 211.0842. C₁₀H₁₃NO₄ requires M⁺, 211.0845). ¹H NMR δ 5.93, q, J = 1.37 Hz, 1H; 5.73, q, J = 0.8 Hz, 1H; 4.18, q, J = 7.1 Hz, 2H; 2.48, d, J = 0.8 Hz, 3H; 2.43, d, J = 1.37 Hz, 3H; 1.26, t, J = 7.1 Hz, 3H. ¹³C NMR δ 166.1, 165.7, 165.3, 154.2, 119.9, 105.6, 60.6, 14.4, 14.2, 14.1. υmax 1713, 1659, 1622 cm⁻¹. Mass spectrum (m/z) 211 (M⁺, 1%), 196 (3), 165 (14), 150 (10), 127 (13), 113 (19), 99 (33), 88 (26), 82 (41), 69 (25), 55 (28), 43 (100).

The second fraction contained ethyl 3-(3-methyl-5-oxo-2,5-dihydroisoxazol-2-yl)but-2-enoate 13f, which was obtained as a yellow oil (0.075 g, 41%). (Found: M⁺, 211.0842. C₁₀H₁₃NO₄ requires M⁺, 211.0845). ¹H NMR δ 5.71, q, J = 0.96 Hz, 1H; 5.14, q, J = 0.82 Hz, 1H; 4.15, q, J = 7.1 Hz, 2H; 2.48, d, J = 0.96 Hz, 3H; 2.34, d, J = 0.82 Hz, 3H; 1.25, t, J = 7.1 Hz. ¹³C NMR δ 167.8, 165.7, 158.8, 147.6, 107.6, 92.0, 60.3, 15.3, 14.7, 14.1. υmax 1750, 1710, 1626, 1575 cm⁻¹. Mass spectrum (m/z) 211 (M⁺, 88%), 195 (3), 182 (5), 166 (100), 150 (16), 139 (66), 122 (51), 110 (16), 99 (17), 82 (73), 67 (45), 54 (35), 39 (31).

Flash vacuum pyrolysis of 13f

Pyrolysis (450 °C, 150 °C, 0.1mmHg) of 13f (0.095 g, 0.45 mmol) gave ethyl 2,5-
dimethylpyrrole-3-carboxlate 15f as colourless crystals (0.07 g, 93%), mp. 116 °C (lit.19 113 °C). (Found: M⁺, 167.0947. C₉H₁₅NO₂ requires M⁺, 167.0946). ¹H NMR δ 8.33, bs, 1H, NH; 6.18, dq, J = 0.96, 2.9 Hz, 1H; 4.23, q, J = 7.1 Hz, 2H; 2.46, s, 3H; 2.17, d, J = 0.96 Hz, 3H; 1.32, t, J = 7.1 Hz, 3H. ¹³C NMR δ 165.6, 134.3, 125.6, 111.5, 107.3, 59.2, 14.5, 13.1, 12.5. v_max 1689, 1437, 1224, 1087 cm⁻¹. Mass spectrum (m/z) 167 (M⁺, 68%), 138 (100), 122 (23), 105 (3), 94 (8).

**Ethyl 3-(5-oxo-3-methyl-2,5-dihydroisoxazol-2-yl)-3-phenylpropenoate (13g)**

3-Methylisoxazol-5(4H)-one (1.0 g, 10.1 mmol), ethyl phenylpropiolate (1.76 g, 10.1 mmol) and triethylamine (1.02 g, 10.1 mmol) were refluxed in ethanol (30 mL) for 16 h. The product was purified by radial chromatography (20% ethyl acetate/light petroleum), to give two fractions. The first fraction contained unreacted ethyl phenylpropiolate (0.777 g). The second fraction contained ethyl 3-(5-oxo-3-methyl-2,5-dihydroisoxazol-2-yl)-3-phenylpropenoate 13g which was obtained as an orange oil (1.093 g, 71%, based on unreacted starting material). (Found: M⁺, 273.0989. C₁₅H₁₅NO₄ requires M⁺, 273.1001). ¹H NMR δ 7.30-7.38, m, 5H; 6.15, s, 1H; 5.09, q, J = 0.7 Hz, 1H; 4.13, q, J = 7.1 Hz, 2H; 1.97, d, J = 0.7 Hz, 3H; 1.20, t, J = 7.1 Hz, 3H. ¹³C NMR δ 169.4, 163.1, 161.1, 143.7, 133.5, 131.3, 128.9, 127.0, 115.5, 88.0, 60.9, 13.8, 12.4. v_max 1758, 1718, 1623, 1576, 1448, 1368, 1282 cm⁻¹. Mass spectrum (m/z) 273 (M⁺, 81%), 228 (36), 200 (18), 175 (80), 156 (15), 147 (100), 131 (13), 116 (18), 103 (94), 91 (26), 69 (36).

**Flash vacuum pyrolysis of 13g**

Pyrolysis (450°C, 150°C, 0.01 mmHg) of 13g (0.065 g, 0.23 mmol) gave pale brown oil (0.05 g), which was purified by radial chromatography (10% ethyl acetate/light petroleum), to give two fractions. The first fraction contained ethyl 5-methyl-2-phenylpyrrole-3-carboxylate 15g, which was obtained as a colourless oil (1.093 g, 19%). (Found: M⁺, 229.1102. C₁₄H₁₅NO₂ requires M⁺, 229.1103). ¹H NMR δ 8.13, bs, 1H, NH; 7.55-7.59, m, 2H; 7.29-7.41, m, 3H; 6.40, dq, J = 0.82, 3 Hz, 1H; 4.19, q, J = 7.0 Hz, 2H; 2.56, s, 3H; 1.48, t, J = 7.0 Hz, 3H. ¹³C NMR δ 165.0, 135.9, 132.3, 128.8, 128.0, 127.9, 127.6, 112.2, 109.6, 59.5, 14.3, 12.7. v_max 1672 cm⁻¹. Mass spectrum (m/z) 229 (M⁺, 90%), 201 (23), 184 (100), 170 (3), 156 (13), 141 (3), 128 (10), 104 (7), 77 (10).

The second fraction, colourless oil (0.02 g, 38%) has not yet been identified. (Found: M⁺, 229.1092. C₁₄H₁₅NO₂ requires M⁺, 229.1103). ¹H NMR δ 7.84-7.87, m, 2H; 7.29-7.44, m, 3H; 7.04, s, 1H; 4.21, q, J = 7.0 Hz, 2H; 2.56, s, 3H; (OH unsighted). ¹³C NMR δ 152.1, 149.6, 144.4, 139.6, 139.3, 128.6, 128.2, 126.8, 102.5, 64.7, 18.2, 14.6. v_max 1473, 1078 cm⁻¹. Mass spectrum (m/z) 229 (M⁺, 100%), 214 (6), 201 (56), 185 (17), 172 (29), 156 (5), 131 (9), 115 (6), 102 (10), 77 (9).

**Acknowledgements**
The authors are grateful for support of this project by the Australian Research Council. M.C. acknowledges the award of a Flinders University Research Scholarship.

References and Notes

12. We thank Dr D.S. Millan for this observation.