

# Trapping reactions of 1-methoxyfuran *endo*-peroxides with 4-nitrobenzaldehyde oxime. Regio- and stereoselective synthesis of the first oxime *O*-[2,5-dihydro-5-hydroperoxy-2-furyl] ethers

M. Rosaria Iesce,<sup>\*a</sup> Flavio Cermola,<sup>a</sup> Antonio Guitto<sup>a</sup> and Federico Giordano<sup>b</sup>

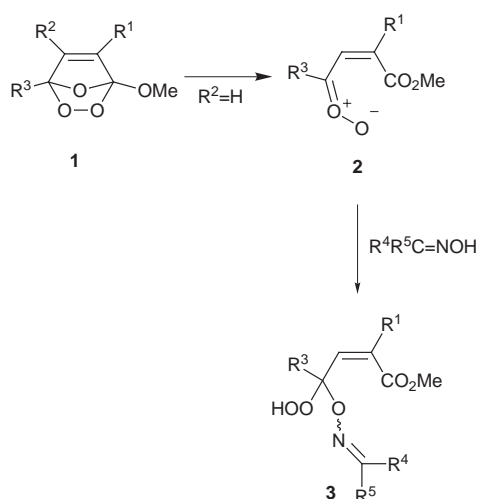
<sup>a</sup> Dipartimento di Chimica Organica e Biologica dell'Università di Napoli Federico II, via Mezzocannone 16, I-80134 Napoli, Italy

<sup>b</sup> Dipartimento di Chimica dell'Università di Napoli Federico II, via Mezzocannone 4, I-80134 Napoli, Italy

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The synthesis of the title compounds by dye-sensitized photooxygenation of 2-methoxyfurans in the presence of 4-nitrobenzaldehyde oxime is described. The crystal structure determination of a derivative is also reported.

The reaction of C-5 unsubstituted *endo*-peroxides **1**, obtained by photooxygenation of the parent 2-methoxyfurans, with various aldo and keto oximes has been reported to afford  $\alpha$ -oxime ether hydroperoxides, such as **3** (Scheme 1).<sup>1,2</sup> These



Scheme 1

compounds are formed through an oxygen nucleophilic trapping reaction of intermediate carbonyl oxides **2** and, depending on the nature of the substituents on the oxime moiety, they thermally rearrange into *N*-hydroperoxyalkyl-nitrones or, sometimes, can be isolated.<sup>2</sup>

We now report that the reaction of *endo*-peroxides **1** with 4-nitrobenzaldehyde oxime (**5**) unexpectedly leads to dihydrofurans **6** in moderate to good yields.

## Results and discussion

In the presence of two equivalents of **5**, tetraphenylporphyrin-sensitized photooxygenation of furan **4a** in CH<sub>2</sub>Cl<sub>2</sub> at -20 °C led to the dihydrofuran **6a** (26%), mp 103–105 °C (Scheme 2). The structural assignment was based on the appearance of two <sup>13</sup>C NMR signals for quaternary carbons at  $\delta$  114.3 and 122.0; as the latter is compatible with an orthoester function,<sup>†</sup>

<sup>†</sup> The chemical shifts of polyoxygenated carbons for structurally related dihydrofurans were found in the range  $\delta$  121–122 ppm.<sup>3</sup>

the signals can be attributed to C-5 and C-2, respectively. Formation of **6a** indicated that carbonyl oxide **2a** was not an intermediate of the reaction<sup>‡</sup> and that *endo*-peroxide **1a** was trapped by oxime **5** before rearranging into **2a**. This result was especially surprising since structurally related dihydrofurans were never obtained, even by methanol addition, starting from C-5 unsubstituted *endo*-peroxides which lead to open chain hydroperoxides *via* the corresponding carbonyl oxides.<sup>§</sup>

Similar results were obtained using furans **4b–e**. However, when oxygenation was extended to fully substituted furans **4f–i** whose *endo*-peroxides do not open into carbonyl oxides,<sup>7</sup> the reaction was successful only for **4f,g** (Scheme 2).<sup>¶</sup> All compounds **6** obtained were characterized by spectroscopic and/or analytical data. The structure was confirmed by X-ray crystallographic analysis of **6c** which further highlighted the *cis* relationship between the OOH function and oxime moiety (Fig. 1).<sup>||</sup> It is noteworthy that, as shown in Fig. 1, the molecular structure is stiffened and energetically stabilized by the intramolecular O(5)–H...N(1) H-bond [O(5)...N(1) 2.94(2) Å, H...N(1) 2.04(1) Å, O(5)–H...N(1) 155(2)°]. This internal hydrogen bond is responsible for the unusually low signal ( $\delta$  11.05) of the OOH proton in the <sup>1</sup>H NMR spectrum in comparison with those ordinarily observed (*ca.*  $\delta$  8–9); the same interaction is also present in all other compounds **6**, as indicated by the values of the OOH chemical shifts ( $\delta$  10.91–11.52).

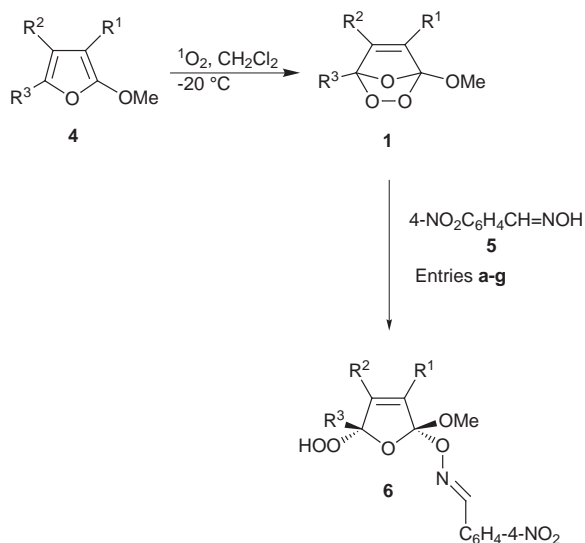
In each reaction mixture, no evidence of any other isomer different from **6** was obtained.

<sup>‡</sup> Neither spectroscopic nor chromatographic evidence was obtained for the presence of the corresponding oxime ether hydroperoxide nor related deriving products. In addition to polymeric material, the only identifiable products were those usually formed in polar media.<sup>3,4</sup>

<sup>§</sup> Formation of dihydrofurans structurally related to **6** by methanol addition is typical for 1,4-dialkyl or 1,4-diaryl *endo*-peroxides<sup>5</sup> as well as for C-5 substituted 1-alkoxy derivatives,<sup>6,7</sup> which do not open into carbonyl oxides; as regards 1-alkoxy derivatives unsubstituted at C-5 thermal rearrangement into carbonyl oxides is faster than the trapping reaction.<sup>7</sup>

<sup>¶</sup> For entries **h,i** only products deriving from thermal conversion of *endo*-peroxides **1 h,i** were formed.<sup>8</sup>

<sup>||</sup> The geometric features closely agree with those found in the crystal structure of 2,5-dimethyl-2-hydroperoxy-5-methoxy-2,5-dihydrofuran obtained by methanol addition to the *endo*-peroxide of 2,5-dimethylfuran where, however, the hydrogen bond formed by the hydroperoxy group is intermolecular.<sup>9</sup>

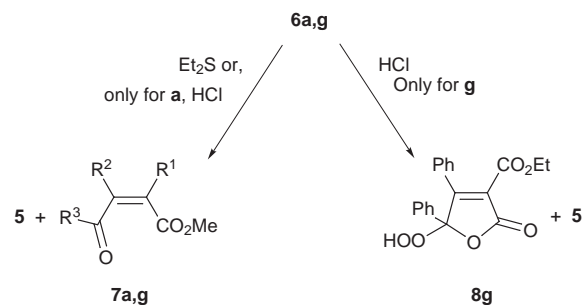


Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield <sup>a</sup> (%) of <b>6</b>
a	CO <sub>2</sub> Me	H	Ph	26
b	CO <sub>2</sub> Me	H	4-Me-C <sub>6</sub> H <sub>4</sub>	10
c	CO <sub>2</sub> Me	H	3-MeO-C <sub>6</sub> H <sub>4</sub>	38
d	CO <sub>2</sub> Me	H	4-Br-C <sub>6</sub> H <sub>4</sub>	35
e <sup>b</sup>	COMe	H	Ph	12
f	CO <sub>2</sub> Me	Me	Ph	51
g	CO <sub>2</sub> Et	Ph	Ph	80
h	H	CO <sub>2</sub> Me	Ph	—
i	CO <sub>2</sub> Me	CO <sub>2</sub> Me	Ph	—

<sup>a</sup> Isolated product. <sup>b</sup> Obtained with a purity of 85% (<sup>1</sup>H NMR).

As shown in Scheme 2, the formation of **6** is strictly dependent on the nature of the substituent at C-5 of the *endo*-peroxides **1**; it takes place, however, only using oxime **5**.<sup>\*\*</sup> It is likely that the interaction of the fairly electrophilic OH hydrogen of **5** with the peroxy group facilitates the breakage of the C-1–O-2 bond, which only occurs when the developing positive charge at C-1 is not destabilized by an electron-withdrawing group at C-5; concomitantly, as indicated by the stereochemical trend, the oxime oxygen attacks C-1 on the same side of the leaving OOH group and, for entries **a–e**, this occurs more rapidly than the rearrangement into the corresponding carbonyl oxides. Electronic effects due to the methyl and phenyl group may account for the higher yields of **6f,g** than those of **6a–e**.

Compounds **6** are the first oxime-adducts of furan *endo*-peroxides and, as exemplified by derivatives **6a,g**, have chemical properties similar to closely related hydroperoxidic 2,5-dihydrofurans.<sup>6,10</sup> Reduction with Et<sub>2</sub>S proceeded quickly at room temperature yielding a clean product mixture of oxime and ester **7** quantitatively.<sup>10</sup> Both the latter compounds were also obtained by acid hydrolysis of C-4 unsubstituted **6a** while **6g** led to 5-hydroperoxyfuran-2(5*H*)-one **8g** as well as to oxime **5** (Scheme 3).<sup>6</sup>



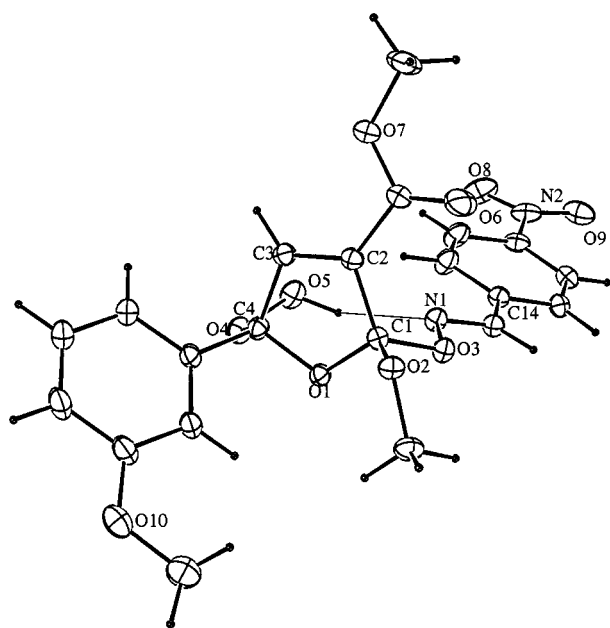
In conclusion, the present work reports the first trapping reaction of C-5 unsubstituted 1-methoxyfuran *endo*-peroxides by a protic species, namely 4-nitrobenzaldehyde oxime. The reaction may also be performed with fully substituted derivatives with the exception of those bearing an electron-withdrawing group at C-5. It represents a one-pot method for the regio- and stereoselective synthesis for dihydrofurans **6** which are the first examples of cyclic monooxime ortho esters of hydroperoxy compounds.

## Experimental

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The IR spectra were obtained on a Perkin-Elmer 1760X-FT spectrophotometer using CHCl<sub>3</sub> as solvent. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 250 MHz and 62.8 MHz respectively on a Bruker AC-250 spectrometer using CDCl<sub>3</sub> as solvent and TMS as internal standard. *J* Values are given in Hz. Elemental analyses were obtained using a Carlo Erba EA 1108-Elemental Analyzer. CH<sub>2</sub>Cl<sub>2</sub> was anhydrous. Silica gel (0.063–0.2 mm Macherey-Nagel) and light petroleum (bp 40–60 °C) were used for column chromatography. 4-Nitrobenzaldehyde oxime and tetraphenylporphyrin (TPP) (Fluka) were used without purification. The furans **1a,e,h,i**,<sup>3</sup> **1b**,<sup>11</sup> **1c**,<sup>10</sup> **1d**,<sup>4</sup> **1f,g**<sup>6</sup> were prepared according to literature methods.

**CAUTION:** Since organic peroxides are potentially hazardous compounds, they must be handled with care. No

<sup>\*\*</sup> Control experiments showed that when the oxygenation of **1a** was carried out in the presence of 4-methyl- or 4-bromobenzaldehyde oxime no related dihydrofuran was formed and the results were similar to those obtained for benzaldehyde oxime.<sup>2</sup>



**Fig. 1** Molecular structure of **6c** with key atoms numbered. Relevant bond lengths (Å) and angles (°), including H-bond parameters, are as follows. O(1)–C(1) 1.415(2), O(1)–C(4) 1.435(2), O(2)–C(1) 1.375(2), O(3)–N(1) 1.412(2), O(3)–C(1) 1.421(2), O(4)–O(5) 1.461(2), O(4)–C(4) 1.414(2), N(1)–C(14) 1.267(3), C(1)–C(2) 1.503(3), C(2)–C(3) 1.317(3), C(3)–C(4) 1.496(3); C(1)–O(1)–C(4) 110.4(2), N(1)–O(3)–C(1) 110.0(2), O(5)–O(4)–C(4) 109.1(2), O(3)–N(1)–C(14) 109.8(2), O(1)–C(1)–O(2) 112.4(2), O(1)–C(1)–C(2) 104.7(2), O(2)–C(1)–C(2) 110.4(2), C(1)–C(2)–C(3) 109.6(2), C(2)–C(3)–C(4) 110.4(2), O(1)–C(4)–O(4) 107.8(2), O(1)–C(4)–C(3) 104.1(2), O(4)–C(4)–C(3) 114.0(2); O(5)···N(1) 2.941(2), H···N(1) 2.04(1), O(5)–H···N(1) 155(2).

particular difficulties were experienced in handling any of the new peroxides reported in this work.

#### Photooxygenation of furans 4a–i in the presence of 4-nitrobenzaldehyde oxime 5: general procedure

Each  $2 \times 10^{-2}$  mol dm<sup>-3</sup> solution of the furans 4a–i (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) and the oxime 5 (166 mg, 1 mmol) after the addition of TPP ( $3.6 \times 10^{-4}$  mmol), was irradiated at  $-20^\circ\text{C}$  with a halogen-superphot lamp (Osram, 650 W). During the irradiation, dry oxygen was bubbled through the solution which was kept at this temperature. When each reaction was complete (120 min), the solvent was removed under reduced pressure at room temp. and the residue analyzed by <sup>1</sup>H NMR. For entries a–e, in addition to the unreacted oxime, the spectra showed the presence of the dihydrofurans 6a–e and the corresponding keto esters 7a–e. Rapid column chromatography†† on silica gel, eluting with light petroleum–diethyl ether (8:2, 1:1), gave mixtures of the oxime and keto esters 7a–e<sup>10</sup> and dihydrofurans 6a–e, successively. For entries f, g <sup>1</sup>H NMR analysis indicated the presence of only dihydrofurans 6f, g which were isolated by chromatography as above.

Neither spectroscopic nor chromatographic evidence was obtained to indicate the presence of 6h, i. The only products present were those formed by thermal conversion of endoperoxides 1h, i, and were identified by comparing spectral data of these mixtures with those obtained in the absence of oxime 5.<sup>8</sup>

**4-Nitrobenzaldehyde oxime O-[2,5-dihydro-5-hydroperoxy-2-methoxy-3-(methoxycarbonyl)-5-phenyl-2-furyl] ether 6a.** Yield 26%; mp 103–105 °C (from hexane–Et<sub>2</sub>O) (Found C, 55.9; H, 4.1; N, 6.6. C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>9</sub> requires C, 55.81; H, 4.22; N, 6.51%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3586, 3250, 1744, 1698, 1530, 1346;  $\delta_{\text{H}}$  3.73 and 3.79 (6 H, 2 × s, 2 × OMe), 7.32 (s) and 7.40–7.70 (m) (8 H, 4-H + ArH), 8.26 (2 H, d, *J* 8.8, ArH); 8.43 (1 H, s, CH=N); 11.04 (1H, br s, OOH);  $\delta_{\text{C}}$  51.6 (q), 52.2 (q), 114.3 (s), 122.0 (s), 124.2 (d), 126.3 (d), 128.3 (d), 128.7 (d), 130.0 (d), 132.6 (s), 134.7 (s), 136.2 (s), 144.8 (d), 149.1 (s), 150.9 (d), 160.5 (s).

**4-Nitrobenzaldehyde oxime O-[2,5-dihydro-5-hydroperoxy-2-methoxy-3-(methoxycarbonyl)-5-(4-methylphenyl)-2-furyl] ether 6b.** Yield 10%; viscous oil (Found C, 56.5; H, 4.3; N, 6.2. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>9</sub> requires C, 56.75; H, 4.54; N, 6.30%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3571, 3224, 1737, 1679, 1526, 1347;  $\delta_{\text{H}}$  2.38 (3 H, s, Me), 3.73 (3 H, s, OMe), 3.80 (3 H, s, OMe), 7.32 (s) and 7.20–7.70 (m) (7 H, 4-H + ArH), 8.27 (2 H, d, *J* 8.8, ArH), 8.43 (s, 1H, CH=N), 11.09 (1 H, br s, OOH);  $\delta_{\text{C}}$  21.2 (q), 51.7 (q), 52.3 (q), 114.5 (s), 122.8 (s), 124.3 (d), 126.2 (d), 128.4 (d), 129.5 (d), 131.8 (s), 132.4 (s), 136.2 (s), 140.2 (s), 145.0 (d), 149.2 (s), 150.6 (d), 160.6 (s).

**4-Nitrobenzaldehyde oxime O-[2,5-dihydro-5-hydroperoxy-2-methoxy-3-(methoxycarbonyl)-5-(3-methoxyphenyl)-2-furyl] ether 6c.** Yield 38%; mp 99–102 °C (from hexane–Et<sub>2</sub>O) (Found C, 54.9; H, 4.7; N, 6.1. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>10</sub> requires C, 54.78; H, 4.38; N, 6.09%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3505, 3227, 1737, 1670, 1526, 1347;  $\delta_{\text{H}}$  3.75, 3.80 and 3.83 (9 H, 3 × s, 3 × OMe), 6.90–7.71 (7 H, m, 4-H + ArH), 8.25 (2 H, d, *J* 8.8, ArH), 8.44 (1 H, s, CH=N), 11.05 (1 H, br s, OOH);  $\delta_{\text{C}}$  51.6 (q), 52.2 (q), 55.2 (q), 111.7 (d), 114.2 (s), 115.8 (d), 118.6 (d), 122.9 (s), 124.2 (d), 128.3 (d), 129.8 (d), 132.4 (s), 136.1 (2 s), 144.8 (d), 149.1 (s), 150.6 (d), 159.8 (s), 160.5 (s).

**4-Nitrobenzaldehyde oxime O-[5-(4-bromophenyl)-2,5-dihydro-5-hydroperoxy-2-methoxy-3-(methoxycarbonyl)-2-furyl] ether 6d.** Yield 35%; 119–121 °C (from hexane–Et<sub>2</sub>O) (Found C, 47.0; H, 3.2; N, 5.5. C<sub>20</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>9</sub> requires C, 47.17; H, 3.36;

N, 5.50%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3575, 3217, 1738, 1670, 1526, 1348;  $\delta_{\text{H}}$  3.72 and 3.80 (6 H, 2 × s, 2 × OMe), 7.24 (1 H, s, 4-H), 7.40–7.70 (6 H, m, ArH), 8.25 (2 H, d, *J* 8.8, ArH), 8.42 (1 H, s, CH=N), 10.91 (1 H, br s, OOH);  $\delta_{\text{C}}$  51.7 (q), 52.3 (q), 113.8 (s), 123.0 (s), 124.3 (d), 124.5 (s), 128.0 (d), 128.4 (d), 131.9 (d), 133.2 (s), 134.0 (s), 136.2 (s), 144.1 (d), 149.3 (s), 150.7 (d), 160.4 (s).

**4-Nitrobenzaldehyde oxime O-[2,5-dihydro-5-hydroperoxy-2-methoxy-3-(1-oxoethyl)-5-phenyl-2-furyl] ether 6e.** Yield 12% (with a purity of 85%, by <sup>1</sup>H NMR);  $\delta_{\text{H}}$  2.40 (3 H, s, Me), 3.75 (3 H, s, OMe), 7.21 (1 H, s, 4-H), 7.40–7.70 (m, ArH), 8.25 (2 H, d, *J* 8.8, ArH), 8.42 (1 H, s, CH=N), 10.94 (1 H, br s, OOH).

**4-Nitrobenzaldehyde oxime O-[2,5-dihydro-5-hydroperoxy-2-methoxy-3-(methoxycarbonyl)-4-methyl-5-phenyl-2-furyl] ether 6f.** Yield 51%; mp 92–94 °C (from hexane–Et<sub>2</sub>O) (Found C, 56.5; H, 4.7; N, 6.2. C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>9</sub> requires C, 56.75; H, 4.54; N, 6.30%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3607, 3179, 1726, 1682, 1526, 1347;  $\delta_{\text{H}}$  2.12 (3 H, s, Me), 3.77 and 3.82 (6 H, 2 × s, 2 × OMe), 7.30–7.70 (7 H, m, ArH), 8.25 (2 H, d, *J* 8.8, ArH), 8.42 (1 H, s, CH=N), 11.36 (1 H, br s, OOH);  $\delta_{\text{C}}$  12.1 (q), 51.5 (q), 51.9 (q), 116.0 (s), 122.9 (s), 124.3 (d), 126.2 (d), 126.4 (s), 128.3 (d), 128.6 (d), 129.7 (d), 135.0 (s), 136.3 (s), 149.2 (s), 150.3 (d), 157.0 (s), 162.0 (s).

**4-Nitrobenzaldehyde oxime O-[3-(ethoxycarbonyl)-2,5-dihydro-5-hydroperoxy-2-methoxy-4,5-diphenyl-2-furyl] ether 6g.** Yield 80%; mp 98–100 °C (from hexane–Et<sub>2</sub>O) (Found C, 62.4; H, 4.7; N, 5.3. C<sub>27</sub>H<sub>24</sub>N<sub>2</sub>O<sub>9</sub> requires C, 62.30; H, 4.65; N, 5.38%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3605, 3223, 1723, 1673, 1526, 1346;  $\delta_{\text{H}}$  0.96 (3 H, t, *J* 7.3, Me), 3.83 (3 H, s, OMe), 4.06 (2 H, m, OCH<sub>2</sub>), 7.25–7.70 (12 H, m, ArH), 8.28 (2 H, d, *J* 8.8, ArH), 8.44 (1 H, s, CH=N), 11.52 (1 H, br s, OOH);  $\delta_{\text{C}}$  13.6 (q), 51.6 (q), 61.1 (t), 116.1 (s), 122.4 (s), 124.4 (d), 126.5 (d), 127.7 (d), 128.2 (d), 128.4 (d), 129.0 (d), 129.2 (d), 129.6 (d), 130.0 (s), 134.8 (s), 136.4 (2 s), 149.2 (s), 150.4 (d), 153.9 (s), 161.4 (s).

#### Reduction of dihydrofurans 6a, g

A solution of 6a (30 mg, 0.07 mmol) in CDCl<sub>3</sub> (0.8 cm<sup>3</sup>) was treated with excess Et<sub>2</sub>S (13 mg, 0.14 mmol). <sup>1</sup>H NMR analysis after 15 min showed only the presence of keto ester 7a and oxime 5 in 1:1 molar ratio, in addition to Et<sub>2</sub>S and Et<sub>2</sub>SO. A similar result was obtained starting from 6g. Keto esters 7a, g were identified by comparison of spectral data with those of authentic samples.<sup>10</sup>

#### Acid hydrolysis of dihydrofurans 6a, g

A solution of 6a (60 mg, 0.14 mmol) in acetone (4 cm<sup>3</sup>) was treated with 2 mol dm<sup>-3</sup> HCl (0.04 cm<sup>3</sup>) and kept at room temp. After 30 min acetone was removed, water was added and the mixture was extracted with CHCl<sub>3</sub>, dried (MgSO<sub>4</sub>) and evaporated. The residue, analyzed by <sup>1</sup>H NMR, showed the presence of keto ester 7a<sup>10</sup> and oxime 5 in 1:1 molar ratio. When 6g was hydrolysed as for 6a, <sup>1</sup>H NMR showed the presence of lactone 8g<sup>6</sup> and oxime 5 in 1:1 molar ratio.

#### Crystal data of 6c

C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>O<sub>10</sub>, *M* = 460.4. Monoclinic, *a* = 11.285(2), *b* = 21.933(2), *c* = 8.829(1) Å,  $\beta$  = 91.60(1)°, *V* = 2184(1) Å<sup>3</sup> (by least-squares refinement of the setting angles of 25 strong reflections with  $27 \leq \theta \leq 30^\circ$ ),  $\lambda(\text{Cu-K}\alpha)$  = 1.5418 Å, space group = *P*<sub>2</sub><sub>1</sub>/*c* (No. 14), *Z* = 4, *D*<sub>c</sub> = 1.40 g cm<sup>-3</sup>, *F*(000) = 960. Colourless crystals recrystallized from hexane–Et<sub>2</sub>O. Crystal dimensions: 0.15 × 0.20 × 0.30 mm,  $\mu(\text{Cu-K}\alpha)$  = 9.23 cm<sup>-1</sup>.

**Data collection and processing.** CAD4 diffractometer, graphite-monochromated Cu-K $\alpha$  radiation,  $\omega/\theta$  scan mode, 4485 unique reflections measured ( $1 \leq \theta \leq 75^\circ$ ,  $\pm h$ , *k*, *l*)

†† All dihydrofurans (especially 6b, 6e and 6f) tended to decompose during column chromatography.

and 3534 with  $I \geq 3\sigma(I)$  were retained in all calculations. Three monitoring reflections, measured every 500, showed insignificant intensity fluctuations.

**Structural analysis and refinement.** The structure was solved by SIR92 package<sup>12</sup> and refined by full-matrix least-squares procedure (CAD-4 Software)<sup>13</sup> minimizing the quantity  $\sum w(\Delta F)^2$  with  $w^{-1} = [\sigma^2(F_o) + (0.02 F_o)^2 + 1.0]$  where  $\sigma$  was derived from counting statistics. All non-hydrogen atoms were refined anisotropically. The H-atoms were placed on the basis of geometric considerations and  $\Delta F$  map suggestions for the hydroxy and methyl groups and included as fixed atoms in the last refinement cycles with isotropic thermal parameters equal to those of the carrier atoms. Final  $R$  (on  $F$ ) and  $R_w$  (on  $F_o^2$ ) values of 0.048 and 0.053,  $S$  ( $F^2$ ) 0.906 for 298 refined parameters. The final Fourier difference map showed no peaks greater than  $\pm 0.2 \text{ e } \text{\AA}^{-3}$ . Final  $\Delta/\sigma$  (max) was 0.005.

All calculations, carried out on a Vax 750 were performed by using the Enraf-Nonius (SDP) set of programs.<sup>13</sup>

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/291.

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work was undertaken at the Centro di Metodologie Chimico-Fisiche, Università di Napoli Federico II.

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