

## A Nitroketene to Nitrile Oxide Transformation

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2,3-Dihydropyrrole-2,3-diones **1** thermally extrude CO, giving imidoylketenes **2**, which cyclise efficiently to 4-quinolones **3**; however, the analogous nitro(imidoyl)ketene **5** eliminates CO<sub>2</sub> and rearranges to the 3-oximino-3*H*-indole **9**, presumably *via* an imidoynitrile oxide **7**.

Ketenes are fascinating molecules of considerable potential as synthetic intermediates.<sup>1</sup> In addition, a number of rearrangements of ketenes has been reported.<sup>2</sup>

Imidoylketenes of the type **2** are conveniently generated by extrusion of CO from 2,3-dihydropyrrole-2,3-diones **1** and, as expected,<sup>3</sup> cyclise to give 4-quinolones **3** in yields of 72–94% on heating **1** in diphenyl ether at 240 °C. The progress of reaction was followed by thin layer chromatography (TLC), which revealed a very pronounced substituent effect on the time needed for completion of the decomposition of **1** (0.25–8 h; see Table 1).<sup>†</sup> Electronegative substituents accelerate the

reaction, and these are also the only ones which permit the direct observation of imidoylketenes **2** on flash vacuum pyrolysis (FVP) of **1**. Thus, FVP of **1a–e** at 500–700 °C (10<sup>-4</sup> mbar) (1 bar = 10<sup>5</sup> Pa) with isolation of the products on a KBr disk at 77 K gave only the quinolones **3**, but in the case of **1f**, a ketene signal at 2138 cm<sup>-1</sup> in the IR spectrum was ascribed to **2f**. This signal disappeared on warming to -75 °C, and at room temperature **3f** alone was isolable. Similarly, 4-benzoyl analogues of **2** (R = C<sub>6</sub>H<sub>5</sub>CO) are observable by IR spectroscopy at 77 K (*ca.* 2122 cm<sup>-1</sup>), but efficiently cyclise to **3** (R = C<sub>6</sub>H<sub>5</sub>CO) on FVP at 650 °C.<sup>6</sup> These benzoyl-(imidoyl)ketenes are interesting enough in their own right as <sup>13</sup>C labelling has demonstrated complete ketene–ketene interconversion [R(PhCO)C=<sup>13</sup>C=O ⇌ R(Ph<sup>13</sup>CO)C=C=O] taking place *via* a 1,3-phenyl shift prior to formation of the quinolone.<sup>6</sup>

From the above, one would expect a 4-nitropyrroledione to decompose very rapidly to a nitroketene. Compound **4** was

<sup>†</sup> All new compounds were characterised by satisfactory elemental analysis (C, H and N) and spectroscopic data.

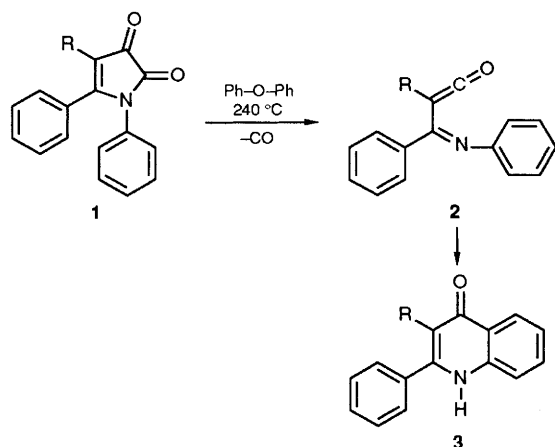
The pyrrolediones **1** are known materials<sup>4</sup> except for **1d**, which was prepared in 80% yield by treatment of **1a** with *N*-bromosuccinimide (NBS) in benzene for 30 min; dark red crystals m.p. 221–223 °C (from toluene). The 4-quinolones **3a–b** and **3d–f** were identified by m.p. and spectral comparison with authentic materials,<sup>5</sup> and **3c** by elemental analytical and spectroscopic data; <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO] δ 0.97 (t, *J* 7 Hz, 3 H), 2.35 (q, *J* 7 Hz, 2 H), 7.18–7.68 (m, 8 H), 8.10 (d, *J* 8 Hz, 1H).

Compound **4**: m.p. 175.5 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.21 (*J* 8 Hz, 6 H), 3.35 (br, 4 H), 7.22–7.62 (m, 5 H); <sup>13</sup>C NMR [(CD<sub>3</sub>)<sub>2</sub>SO] δ 12.9 (CH<sub>3</sub>), 47.7 (CH<sub>2</sub>), 117.5 (C-4), 127.7, 129.7, 130.2, 134.8 (arom.), 160.8 (C-5), 164.6 (C-1), 167.1 (C-2).

Compound **9**: red crystals, m.p. 245–250 °C; UV (EtOH) λ<sub>max</sub> 440 nm; IR (KBr) 2965w, 2930w, 2550br, 1840br, 1590m, 1562s, 1477m, 1447m, 1404m, 1360m, 1325m, 1278m, 1243m, 1192m, 1095m, 1026s, 895w cm<sup>-1</sup>; <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO] δ 1.16 (t, *J* 7 Hz, 6 H), 3.70 (m, 4 H), 6.78 (t, *J* 7.5 Hz, 1 H), 6.89 (d, *J* 7.5 Hz, 1 H), 7.18 (t of d, <sup>1</sup>*J* 7.5 Hz, <sup>2</sup>*J* 1.2 Hz, 1 H), 7.88 (d, *J* 7.5 Hz, 1 H); MS (EI) *m/z* 217 (100), 200 (89), 185 (17), 172 (21), 157 (25), 144 (52), 131 (17), 117 (15), 102 (20); HRMS calcd. for C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O 217.12142; found: 217.1215.

Table 1

Compound <b>1</b>	R	Reaction time/h	Yield of <b>3</b> (%)
<b>a</b>	H	3	94
<b>b</b>	Me	8	90
<b>c</b>	Et	8	92
<b>d</b>	Br	5	72
<b>e</b>	CN	0.5	83
<b>f</b>	CO <sub>2</sub> Et	0.25	91

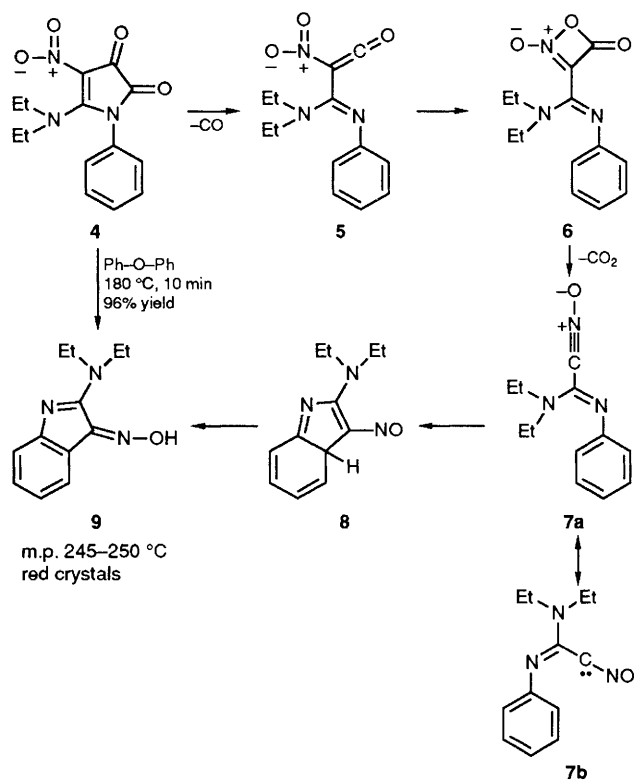


prepared in 40% yield by treatment of 5-methylthio-2,3-dihydro-4-nitro-1-phenylpyrrole-2,3-dione<sup>7</sup> in diethyl ether with diethylamine.† Indeed, **4** decomposed quantitatively and rapidly on heating at 180 °C in diphenyl ether. The reaction was complete in 10 min, when the evolution of gas ceased. Compound **4** was too involatile for an FVP investigation of its decomposition, but isolation of the gases of decomposition on a cryostat at 20 K demonstrated that both CO and CO<sub>2</sub> were formed (2138 and 2340 cm<sup>-1</sup>). The reaction in diphenyl ether yielded a red, crystalline compound in a state of high purity after cooling to room temperature and dilution with hexane. The crude yield was 96%, and after recrystallization from ethanol 82%. The mass spectrum indicated that CO and CO<sub>2</sub> had been lost, and the spectroscopic data were in agreement with the 3-oximino-3*H*-indole structure **9**,† which was confirmed by X-ray crystallography.‡

A rationale for the formation of **9** is set out in Scheme 1. Compound **4** extrudes CO in the normal way to furnish the nitroketene **5**. An electrocyclic reaction involving the nitro and ketene groups leads to the unusual 1,2-oxazet-4-one-*N*-oxide **6**, which eliminates CO<sub>2</sub> to yield the imidoylnitrile oxide **7**. Cyclization to **8** and tautomerization gives the final product **9**. The cyclization of **7** to **8** can be seen, formally, as a reaction of the nitrosocarbene canonical structure of the nitrile oxide, **7b**, in much the same way that nitrile imines can behave like azocarbenes and cyclize to indazoles.<sup>8</sup>

Thus, in summary, we have demonstrated the facile generation of imidoylketenes and obtained the first evidence for the existence of a nitroketene **5** as well as its transformation into a nitrile oxide **7**. Use of different substituents on the pyrrole nitrogen in **4**, in order to prevent cyclization, may be expected to lead to new chemistry of imidoylnitrile oxides related to **7**. In the accompanying communications we show that imidoylketenes are capable of further intriguing rearrangements.

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Scheme 1

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‡ Crystal data for **9**: C<sub>12</sub>H<sub>15</sub>N<sub>3</sub>O, *M* = 217.1, monoclinic, space group *P*2<sub>1</sub>/*a*, *a* = 9.923(6), *b* = 16.851(3), *c* = 13.831(8) Å, β = 97.72(3)°, *U* = 2292(2) Å<sup>3</sup>, *F*(000) = 928 electrons, *Z* = 8, *D*<sub>c</sub> = 1.258 g cm<sup>-3</sup>, μ (Mo-Kα) = 0.8 cm<sup>-1</sup>, Mo-Kα radiation (λ = 0.71073 Å). Crystal size 0.32 × 0.16 × 0.12 mm, colourless plate, *T*, 298 K.

Data were collected on an Enraf-Nonius CAD4 four-circle diffractometer by theta scan type, within the limits 1 < θ < 25°. The structure was solved by direct methods on the basis of 1171 unique reflections with *I* > 2.5σ(*I*); *R* = 0.0650, *R*' = 0.0620, *s* = 2.70. Tables of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.