

Methyleneketene–Imidoylketene–Oxoketenimine Rearrangements

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Methyleneketenes **2** and imidoylketenes **4**, generated from Meldrum's acid derivatives **1** and 2,3-dihydropyrrole-2,3-diones **3**, respectively, both rearrange thermally to oxoketenimines **5**; the imidoylketene–oxoketenimine rearrangement is reversible and much accelerated by electropositive migrating groups (SMe).

A number of fascinating ketene rearrangements has been reported.^{1–4} We have shown by ¹³C labelling that α -oxo-ketenes undergo a ketene–ketene rearrangement involving a 1,3-shift of an aryl group [eqn. (1), R = aryl, X = O], but this reaction does not take place for R = Me.⁵

Furthermore, we have reported indirect evidence for a dramatic acceleration of this rearrangement when R is an electron rich methylthio or dimethylamino group [eqn. (1), X = NR'].³ We now report the first direct evidence for this type of process, interconverting imidoylketenes and oxoketenimines.

Ketenes were generated by flash vacuum pyrolysis (FVP) of 2,3-dihydropyrrole-2,3-diones **3** and Meldrum's acid derivatives **1**.[†] Isolation of the products of FVP of **3a** (400–600 °C; 10^{–4} mbar) as neat solids at 77 K did not permit the detection of imidoylketene **4a** by IR spectroscopy. Instead, only the ketenimine **5a** was observed by a strong absorption at 2076 cm^{–1}. This compound was essentially pure under these conditions (see below). However, trapping of the products of FVP of **3a** (500 °C) in Ar matrix at 18 K permitted the observation of a sharp band at 2132 cm^{–1}, *i.e.* in the region typical of ketenes, which we assign to imidoylketene **4a**. CO

appeared at the same time at 2138 cm^{–1}, and a strong absorption at 2076 cm^{–1} due to **5** was still present.

Further evidence for the nature of compound **4a** was adduced by generation of the same species [2132(s) cm^{–1}] from the Meldrum's acid derivative **1a** at 400–500 °C/10^{–4} mbar. Peaks due to CO₂, acetone, and **5a** (2076 cm^{–1}) were again observed in the Ar matrix IR spectra. At FVP temperatures above 500 °C, the 2132 cm^{–1} species decreased, and the 2076 cm^{–1} species increased in intensity. The methyleneketene **2a**, expected to be the primary product of pyrolysis of **1a**, was not directly observable under these conditions due to its rapid tautomerisation to **4a** or to initial formation of **4a** via an imidoyl(carboxy)ketone.⁶ Other examples of facile 1,3-shifts converting aminomethylene-ketenes to imidoylketenes have been reported.^{2,6}

The thermolysis of **1a** and **3a** to a species C₅H₇NOS was monitored very instructively by mass spectrometry, using an FVP apparatus directly attached to the ion source of a Kratos MS25RFA mass spectrometer.^{7a} The starting material **1** was consumed completely at an FVP temperature of 425 °C. The intermediates C₅H₇NOS (*m/z* 129.0249; calcd. 129.02479) reached a first maximum at 375 °C, and a second at 575 °C. In the FVP of **3**, the starting material was completely consumed at 550 °C, with concomitant formation of the C₅H₇NOS species (*m/z* 129.0249; maximum intensity at 475 °C). The higher temperature required here explains why it is more difficult to detect the imidoylketene **4a** prior to its rearrangement to ketenimine **5a**.

[†] Compound **1a** was prepared by treatment of 5-(bis(methylthio)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione with 1.1 equiv. of methylamine in ethanol (room temperature, 12 h) according to the general procedure:³ yield 78%; m.p. 120–125 °C; ¹³C NMR (CDCl₃) δ 18.33 (SCH₃), 26.04 (CH₃), 32.37 (NCH₃), 83.05 (C-5), 102.64 (C-2), 163.77 (C-4, C-6), 179.85 (C-7); ¹H NMR (CDCl₃) δ 1.68 (s, 6 H; 2 CH₃), 2.56 (s, 3 H, SCH₃), 3.22 (d, *J* 5 Hz, 3 H, NCH₃), 9.86 (br, 1 H, NH); HRMS calcd. for C₉H₁₃NO₄S 231.05644; found: 231.0559.

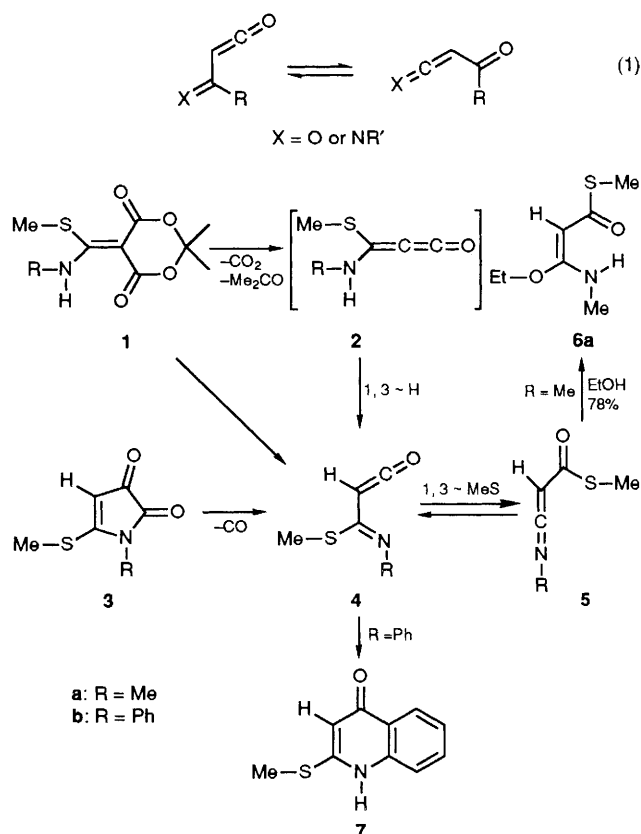
Compound **3a** was prepared in 62% yield from *N,S*-dimethylthioacetamide and oxalyl chloride (1 : 1) in the presence of triethylamine (2 equiv.); room temperature; 30 min; red crystals, m.p. 179–180 °C; ¹H NMR (CDCl₃) δ 2.57 (s, 3 H, SCH₃), 3.16 (s, 3 H, NCH₃), 5.31 (s, 4 H); satisfactory C, H and N analysis.

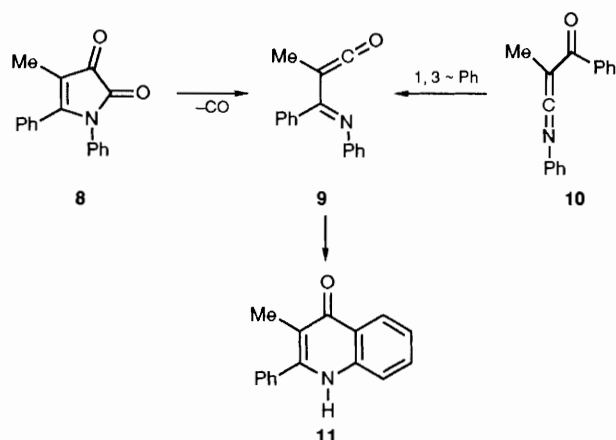
Compound **3b** similarly: 86%; yellow crystals, m.p. 162–163 °C; ¹H NMR (CDCl₃) δ 2.51 (s, 3 H, SCH₃), 5.50 (s, 1 H), 7.20–7.50 (m, 5 H); satisfactory C, H, N analysis.

Compound **5a**: IR (77 K) ν_{\max} 3048w, 3005w, 2932w, 2079s, 1633m, 1411m, 1310w, 1175w, 1128w, 1120w, 1042m, 965w, 869w, 815w cm^{–1}; IR (Ar matrix, 18 K) ν_{\max} 3072w, 3011w, 2951w, 2085sh, 2076s, 2072sh, 1666s, 1415m, 1175w, 1123w, 1110m, 1106m, 1036, 1029m, 961w, 883w, 828w, 821w cm^{–1}; IR (CCl₄, 20 °C; spectrum disappears in 5 min) ν_{\max} 2070, 1653, 1412, 1035 cm^{–1}; ¹H NMR (CD₂Cl₂, –60 °C) δ 2.23 (s, 3 H, SCH₃), 3.42 (d, *J* 2.05 Hz, 3 H, NCH₃), 4.62 (q, *J* 2 Hz, 1 H, CH); ¹³C NMR (CD₂Cl₂, –60 °C) δ 11.34 (q, *J* 142 Hz; SCH₃), 36.17 (dq, *J* 144 Hz, *J* 2.2 Hz; NCH₃), 57.71 (d, *J* 175 Hz; CH), 164.60 (m; CO), 188.97 (m; C=N); HRMS: see text.

Compound **6a**: colourless oil, decomp. after several days at room temperature; IR (film) 3265w, 2927m, 1735w, 1643s, 1576s, 1474m, 1428m, 1241s, 1168s, 1093m, 1033m, 965w cm^{–1}; ¹H NMR (CD₂Cl₂) δ 1.21 (t, *J* 7.0 Hz, 3 H; CH₂CH₃), 2.32 (s, 3 H, SCH₃), 2.95 (d, *J* 5.3 Hz, 3 H, NHCH₃), 4.04 (q, *J* 7.0 Hz, 2 H; OCH₂), 4.39 (s, 1 H; CH), 8.82 (br, 1 H; NH); the doublet at 2.95 ppm collapses to a singlet on addition of D₂O; ¹³C NMR (CD₂Cl₂) δ 14.49 (q, *J* 142 Hz; SCH₃), 14.82 (qt, *J* 124 Hz, *J* 2 Hz; CH₂CH₃), 30.29 (q, *J* 138 Hz; NCH₃), 58.73 (tq, *J* 146 Hz, *J* 4 Hz; OCH₂CH₃), 77.18 (d, *J* 168 Hz; CH), 167.53 and 169.21 (2m, C=CH and CO); MS (EI) 175 (M⁺, 64), 142 (15), 130 (49), 128 (99), 88 (26), 82 (100); HRMS calcd. for C₇H₁₃NO₂S 175.06662; found: 175.0667.

Compound **7** had spectroscopic properties identical with those reported:¹⁰ m.p. 225–226 °C (lit.¹⁰ 220–222 °C).





Warm-up experiments on ketenimine **5a** indicated that this compound was stable until *ca.* 0°C. Therefore, **5a** was dissolved in CD₂Cl₂ below -50°C, and ¹H and ¹³C NMR spectra were recorded at -60°C.†

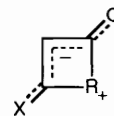
The sample of **5a** was very pure (>90%) as obtained by FVP of **3a** at 600°C/5 × 10⁻⁴ mbar. The NMR spectra were unchanged at -30°C, but irreversible changes took place at 0°C, and **5a** disappeared completely on warming to room temperature. For further identification of **5a**, a separate sample was washed from the 77 K cold finger with CHCl₃ containing 1% ethanol. The resulting product was purified by flash chromatography to give thioester **6a** in 78% yield.† Only one isomer was present, presumably due to intramolecular H bonding. The characterizations of **5a** and **6a** were quite important since electropositively substituted methylene-ketenes such as **2** can also be expected to be relatively stable;⁷ hence, it was mandatory to establish that **5** and not **2** were being isolated.⁸

The 1-phenylpyrroledione **3b** was similarly examined. Decomposition with CO elimination started at *ca.* 350°C. At 400–500°C both a ketene (2122 cm⁻¹) and a ketenimine (2045 cm⁻¹) were observable in the 77 K IR spectra, but the quinolone **7** was detectable already at 420°C and became the sole product at 600°C. Decomposition of **3b** in diphenyl ether at 220°C for 15 min gave **7** in 100% yield.† Other examples of cyclization of imidoalkenes to quinolones have been reported.^{2,9} The detectability of a ketenimine **5b** and the ultimate and quantitative formation of **7** implies that the reaction **4** ⇌ **5** is reversible.

Compound **7** was also obtained by solution thermolysis of **1b**.¹⁰ This reaction presumably leads to **2b** as the first intermediate, which again was not directly observed.

The reversibility of the imidoalkene-oxoketenimine rearrangement was further illustrated in the FVP of **8** and **10** (700°C/10⁻⁴ mbar); both gave quinolone **11** in high yield (95 and 80%, respectively).¹¹

In summary, ketene-ketene rearrangements of the type shown in eqn. (1) are facile for R = SCH₃ (X = NR'), taking place under FVP conditions around 400°C. For R = Ph (X = NPh, **10**; or X = O¹) the reaction requires temperatures of *ca.* 700°C for completion, and for R = Me it does not take place at all, even at 1000°C.⁵ This is in agreement with a four-membered transition state or intermediate:



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- 8 We are carrying out further investigations on ketenes related to **2**, viz. MeS(RNH)CCCO, and the corresponding diamino compounds Me₂N(RNH)CCCO (or the isomeric imidoalkenes), which at temperatures above 600°C and 500°C eliminate MeSH and Me₂NH, respectively, to furnish RNC₃O (R = C₆H₅ or CH₃): C. O. Kappe, T. Mosandl, R. Flammang and C. Wentrup, unpublished results; we are also investigating non-tautomerisable methyleneketenes such as (RS)₂CCCO, which can be handled below -60°C: P. Kambouris and C. Wentrup, unpublished results.
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