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Imidoylketene - Oxoketenimine Rearrangement. Facile 1,3-Shift of an Alkoxy Group

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Abstract: Thermal CO extrusion from 2,3-dihydropyrrole-2,3-dione **3** generates imidoylketene **4**, which cyclizes to 2-methoxy-4-quinolone (**6**). Using flash vacuum pyrolysis and low temperature IR spectroscopy, it is shown that **4** interconverts with ketenimine **5** prior to cyclization to **6**.

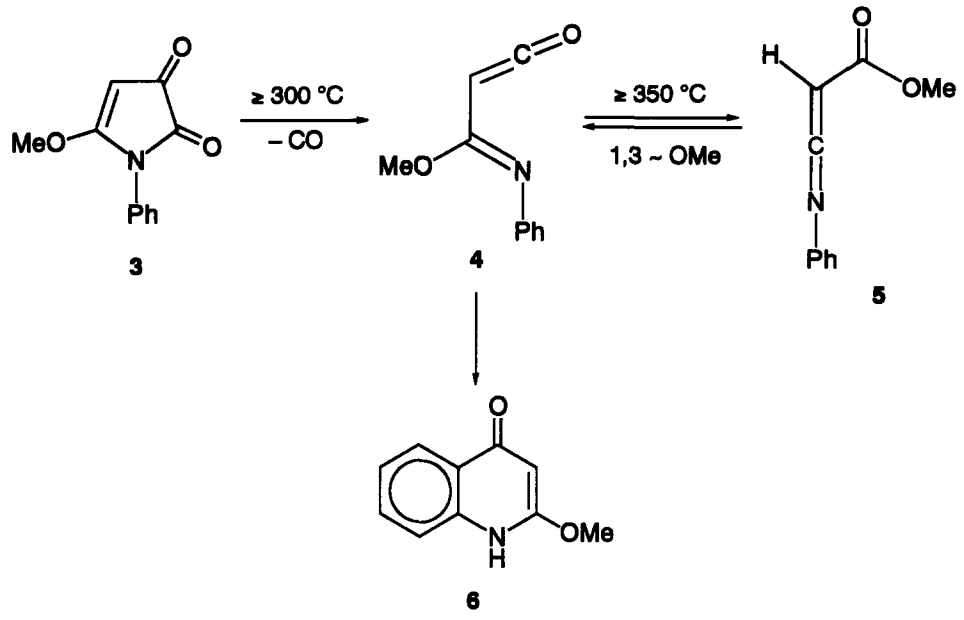
In previous work we have shown that α-oxoketenes (**1a**) undergo a degenerate thermal rearrangement to **2a** by a 1,3-shift of the group R. Imidoylketenes (**1b**) and α-oxoketenimines (**2b**) can interconvert in a similar manner.[1,2]

1 **2**

a: X=O

b: X=NR'

In accordance with experimental observations[2] for R = SMe or NMe_2, these 1,3-migrations are facilitated by electron donation from the migrating group R into the ketene LUMO.[3] Indirect evidence from product studies also indicated that an alkoxy group can participate in this rearrangement.[4] We now report the first direct evidence for the facile 1,3-shift of the methoxy group, interconverting the ketene **4** and the ketenimine **5**.



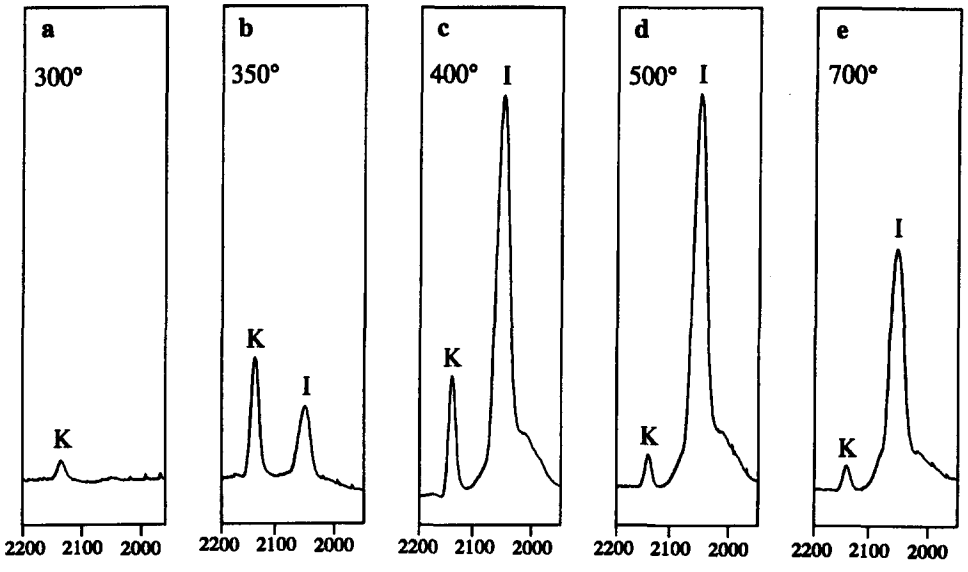


Figure 1. Partial FTIR spectra (1900-2200 cm^{-1} range) of the products (77K) of FVP of **3** at 300 - 700 °C. K = ketene **4** (2135 cm^{-1}); I = ketenimine **5** (2050 cm^{-1}).

5-Methoxy-1-phenyl-2,3-dihydropyrrole-2,3-dione (**3**)[5] was subjected to flash vacuum pyrolysis (FVP) at 250-800 °C (10^{-4} to 10^{-5} mbar) with isolation of the products on a KBr disk at 77 K for FTIR spectroscopic observation. No reaction took place below 300 °C. At 300 °C, a weak band at 2135 cm^{-1} started appearing (Figure 1). This signal increased in intensity till *ca* 400 °C and then decreased, but remained detectable till above 700 °C. At the same time, another band at 2050 cm^{-1} rapidly developed, becoming the major band at 400 °C and remaining so till temperatures above 700 °C (Figure 1). Both of these absorptions started decreasing in intensity above 500 °C, and at 800 °C both had completely disappeared, being replaced by the IR spectrum of 2-methoxy-4-quinolone (**6**).[6]

We assign the first formed intermediate (2135 cm^{-1}) to the ketene **4**, and the second one (2050 cm^{-1}) to the ketenimine **5** for the following reasons.

(i) The expected cyclization product of ketene **4**, i.e. the quinolone **6**, is formed in 97% yield on preparative FVP of **3** at 800 °C (64% at 500 °C).[6]

(ii) The same quinolone **6** was also obtained, albeit in lower yield, by heating **3** (80 mg) in boiling diphenyl ether, (5 mL, 259 °C, 15 min, N_2). Upon cooling, dilution with hexane (30 ml), and column chromatography (SiO_2, ether), **6** was isolated in 36% yield ($R_f = 0.37$).[6]

(iii) The ketenimine **5** is actually isolable at room temperature. In other work, we have generated it from two additional precursors and characterized it by NMR and MS.[7] Therefore, it was possible to identify **5** as a product of the preparative FVP of **3** at 500 °C. Kugelrohr distillation of the product mixture (50 °C, 1.5 x 10^{-5} mbar) gave **5** as a colorless liquid (29%). Chromatography of the residue gave the quinolone **6** in 64% yield.

(iv) FVP of the ketenimine **5** at 800 °C gave the quinolone **6** in 94% yield. By using IR spectroscopic detection, the formation of a small amount of ketene **4** was observed at 450 °C (2125 (w), 2050 (s) cm^{-1} at 77 K).

The absorption intensities of ketene **4** and ketenimine **5** (Figure 1) do not necessarily reflect equilibrium concentrations because **4** is always irreversibly removed from the equilibrium by cyclization to quinolone **6**. In the experiments corresponding to Figure 1 c-e, some quinolone was always formed as well. However, the fact that both peaks are always observable above *ca* 350 °C, starting with either **3** or **5**, demonstrates an extremely facile 1,3-shift of the methoxy group, competing favorably with the cyclization to **6**. Other *N*-arylimidoylketenes often cyclize to quinolones so readily that no ketene can be detected by IR spectroscopy.[2b]

Further experimental work on the imidoylketene—oxoketenimine rearrangement is in progress and will be reported in due course. Further computational work on migratory aptitudes in these and related rearrangements will also be published.[8]

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5. (a) General procedure for the synthesis of 5-alkoxy-1-arylpyrrole-2,3-diones: A solution of 0.1 mmol of the corresponding *N*-arylacetimidic ester, obtained by heating equimolar mixtures of alkyl orthoacetate and the primary aromatic amine,[5b] and 0.2 mmol of dry triethylamine in 50 mL of dry diethyl ether is maintained at 0 °C. A solution of 0.12 mmol of oxalyl chloride in 10 mL of dry diethyl ether is added dropwise during 30 min with vigorous stirring. After 1.5 h at 0 °C, 50 mL of hexane is added, and stirring continued for 30 min at 20 °C. The precipitate is filtered and washed rapidly with ice water to remove the ammonium salt. Thus, **3** was obtained from aniline and triethyl *ortho*acetate. Recrystallization of the crude yellow product from benzene afforded **3** in 83% yield; m.p. 152 °C. Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89. Found: C, 64.99, H, 4.45; N, 6.87. IR (KBr) 1770, 1715, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.09 (s, 3 H, OMe), 4.97 (s, 1 H), 7.2-7.7 (m, 5 H, arom.).
   5-Methoxy-1-(*p*-tolyl)pyrrole-2,3-dione (m.p. 194 °C) and 5-methoxy-1-(*p*-methoxyphenyl)pyrrole-2,3-dione (m.p. 170 °C) were obtained analogously.
   (b) DeWolfe, R.H. *J. Org. Chem.* **1962**, *27*, 490.
6. 2-Methoxy-4-quinolone (**6**): m.p. 170-172 °C. IR (KBr) *ν* 3345, 1635, 1608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.89 (s, 3 H, CH_3), 5.87 (s, 1 H), 7.27 - 8.29 (m, 4 H, arom.); ^{13}C NMR ($CDCl_3$) δ 2.97 (OCH_3), 55.8, 77.2, 118.0, 122.8, 123.4, 125.5, 132.0, 161.4 (C=O). HRMS calcd. for $C_{10}H_9NO_2$: 175.0633; found: 175.0631.
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   Ketenimine **5** had ^1H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 4.59 (s, 1 H), 7.27 - 7.37 (m, 5 H).
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