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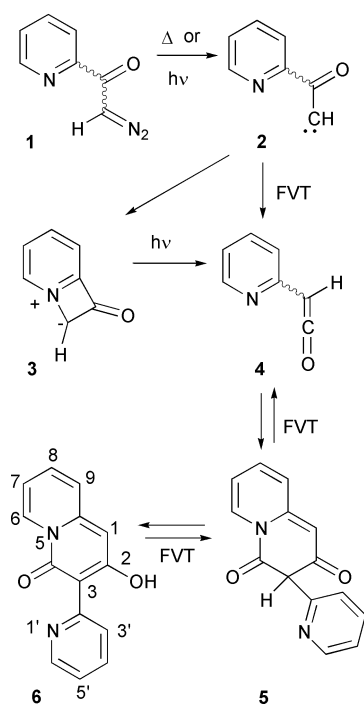
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Quinolizine-2,4-diones **11** are obtained by flash vacuum thermolysis (FVT) of 3-acyl-1,2,3-triazolo[1,5-*a*]pyridines **7**. The reaction takes place *via* methyl- and phenyl(2-pyridyl)ketenes **10**, which are directly observable by infrared spectroscopy in low temperature matrices. FVT of **11** regenerates the ketenes **10**.

## Introduction

We have demonstrated recently that the photolysis of matrix isolated 2-pyridyldiazomethane compound **1** leads to formation of the ylide **3** resulting from an interaction between the putative carbene **2** and the pyridine lone pair (Scheme 1).<sup>1</sup> The ylide is



Scheme 1

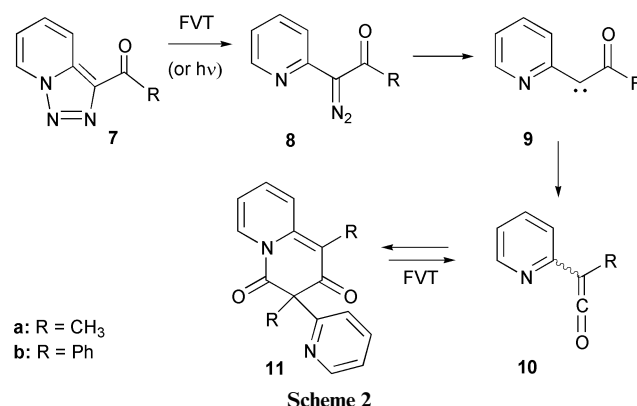
photochemically converted to the ketene **4**, predominantly in the *s-trans* form. Flash vacuum thermolysis (FVT) of **1** gives only the ketene, this time predominantly in the *s-cis* form. The *s-trans* and *s-cis* ketenes can be interconverted photochemically. Under preparative reaction conditions, ketene **4** dimerises to 2-hydroxyquinolizine-4-one **6**, and this reaction is reversible on FVT, regenerating the *s-cis* ketene. The dimerization and dedimerization reactions presumably take place *via* an unobserved quinolizine-2,4-dione **5**. Compound **5** belongs

† Electronic supplementary information (ESI) available: figure of experimental (Ar matrix, 10 K) IR spectrum of **10b** and calculated (B3LYP/6-31G\*) IR spectra of *s-cis*- and *s-trans*-**10b**, and tables of Cartesian coordinates and calculated IR spectra of *s-cis*- and *s-trans*-**10a,b**, 2-(2-pyridyl)benzocyclobutenone, and hypothetical ylides **3** (Me and Ph in place of H). See <http://www.rsc.org/suppdata/p1/b2/b202523j/>

to a very little known class of quinolizinediones (only one previous example),<sup>2</sup> in which the quinolizine moiety is non-aromatic. We now report the first isolation of 3,3-disubstituted quinolizinediones of type **11**, formed by reversible dimerization of 2-pyridylketenes **10**.

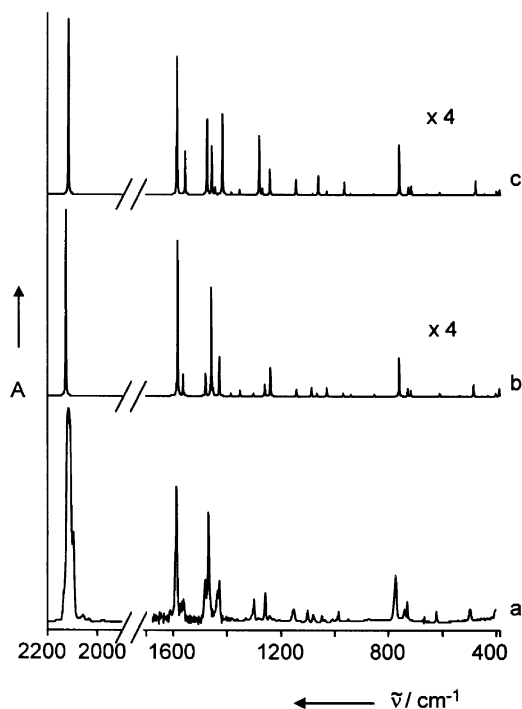
## Results

FVT of triazolopyridines **7** was employed to generate methyl- and phenyl-2-pyridylketenes **10a** and **10b**, presumably taking place *via* the diazo compounds **8** and carbenes **9**. FVT of **7a** at 680–750 °C afforded ketene **10a** without any detectable by-product (Scheme 2). Fig. 1 shows the IR spectrum of the



thermolysate isolated in Ar matrix at 7 K together with the calculated (B3LYP/6-31G\*) IR spectra of the *s-cis* and *s-trans* forms of ketene **10a**. There is excellent agreement between the experimental spectrum and the calculation for the *s-cis* conformer, but a smaller amount of the *s-trans* conformer is probably also present (the shoulder on the low-wavenumber side of the ketene band at 2100–2115 cm<sup>-1</sup>, and the shoulder on the high-wavenumber side of the band at 1588–1594 cm<sup>-1</sup> are assigned to the *s-trans* conformer). This is analogous to the situation with the monosubstituted ketene **4**.<sup>1</sup>

Preparative FVT of **7a** at 650 °C gave a high yield of a crystalline compound identified as the novel quinolizinedione **11a**. Likewise, when the ketene **10a** was isolated at 77 K and then warmed to room temperature, the IR bands of the ketene were replaced by those of the quinolizinedione. **11a** was identified on the basis of its <sup>1</sup>H and <sup>13</sup>C NMR spectra. All proton and carbon signals were unambiguously assigned by means of <sup>1</sup>H–<sup>13</sup>C-COSY (HMBS and HSQC) and selective spin decoupling experiments. The resulting NMR data are in good agreement with the few available data for quinolizine-4-ones.<sup>1,3</sup>



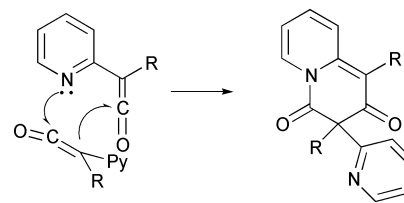
**Fig. 1** IR spectra of methyl(2-pyridyl)ketene **10a**. (a) Experimental spectrum (Ar matrix, 7 K; ketene signals at 2115 and 2100  $\text{cm}^{-1}$ ). (b) and (c) B3LYP/6-31G\* calculated spectra of the *s-cis* and *s-trans* conformers, respectively (scaling factor 0.9613; ketene peaks at 2126 and 2115  $\text{cm}^{-1}$ , respectively). The absorbances of the ketene peaks in the 2100  $\text{cm}^{-1}$  region are attenuated by a factor 4 in each case.

and with estimates based on additivity of substituent effects (Cambridge Scientific Computing, ChemOffice program).

Further evidence for the structure of **11a** is given by the quantitative dedimerisation to **10a** upon FVT at 650 °C, as evidenced by the Ar matrix IR spectrum. This reaction constitutes a [2 + 4]-cycloreversion. Analogous cycloreversions of pyridopyrimidinediones and pyridotriazinediones to 2-pyridylisocyanate and ketenes have been reported previously.<sup>4</sup>

FVT of the benzoyl-substituted triazole **7b** gave the ketene **10b**, which exhibited a very strong absorption at 2117  $\text{cm}^{-1}$  in the Ar matrix IR spectrum. Comparison with the computational data shows very good agreement and indicates a predominance of the *s-cis* isomer, probably with a minor amount of the *s-trans* isomer being present (the experimental and calculated IR spectra are illustrated in the Electronic Supporting Information). † Preparative FVT of **7b** afforded the quinolizinedione **11b** in 75% yield. Again, FVT of **11b** at 650 °C caused quantitative cycloreversion to regenerate ketene **10b** as demonstrated by the Ar matrix IR spectrum.

The dimerisations **10**  $\rightarrow$  **11** are formally [2 + 4]-cycloaddition reactions of imidoylketenes, the pyridine ring behaving as an imine. Since the nitrogen lone pair is likely to be involved in the attack on the ketene LUMO,<sup>5</sup> this cyclodimerisation reaction is likely to be pseudopericyclic and therefore to have a low activation barrier and a more or less planar structure of the transition state.<sup>6</sup> Consequently, the dedimerisation of quinolizinedione **11** to ketene **10** is also likely to be pseudopericyclic.  $\alpha$ -Oxoketenes are known to undergo [2 + 4]-cycloaddition reactions,<sup>7</sup> and calculations on the addition of water and formaldehyde demonstrate that these reactions are pseudopericyclic.<sup>8</sup> Also B3LYP/6-31G\* calculations on the dimerisation and dedimerisation of camphor ketene<sup>9</sup> revealed planar, pseudopericyclic transition structures. Unlike  $\alpha$ -oxoketenes, imidoylketenes are not known to dimerise because they can usually undergo fast intramolecular reactions, *viz.* 1,3-rearrangement to give  $\alpha$ -oxoketenimines, or cyclization to quinolones in the case of *N*-arylimidoylketenes.<sup>10</sup>



The formation of ketenes by photolysis of the triazoles in Ar matrices was also evaluated. Photolysis of **7a** caused formation of ketene **10a** with its main absorptions at 2116 and 2100  $\text{cm}^{-1}$  in the IR spectrum. All the bands expected from Fig. 1a were discernible, but many unassigned bands appeared as well, in particular new bands in the carbonyl group region at 1794 (w) and 1747 (m)  $\text{cm}^{-1}$ . The peak at 1794  $\text{cm}^{-1}$  could conceivably be due to an ylide of type **3** (CH<sub>3</sub> in place of H), formed by rearrangement of carbene **9a** *via* an oxo-carbene–oxirene–oxo-carbene rearrangement.<sup>11</sup> The calculated value for this ylide is 1794  $\text{cm}^{-1}$  (see supplementary data). However, the weakness of the peaks makes assignments hazardous.

The photolysis of the benzoyl derivative **7b** in an Ar matrix afforded only a small amount of ketene (2110 (w)  $\text{cm}^{-1}$ ); instead, a strong carbonyl band appeared at 1770  $\text{cm}^{-1}$ . It was not possible to photo-isomerise this compound to the ketene, thus making it unlikely that it could be an ylide of type **3** (calculated value 1780  $\text{cm}^{-1}$ ). The high value of the carbonyl stretching frequency indicates a strained ketone, and 2-(2-pyridyl)benzocyclobutenone, formed by carbene insertion into an *ortho*-C–H bond of the phenyl group, is a good candidate. The calculated value for this compound is 1790  $\text{cm}^{-1}$  (see supplementary data). Evidently the photo-reactions of these triazoles are complicated and require further investigation. Matrix photolysis of the methoxy analog of **7** (R = OMe) has been reported to afford methoxy(2-pyridyl)ketene (**10**, R = OMe),<sup>12</sup> but our investigations reveal that a different ketene is, in fact, formed, even though FVT at 500 °C gave the desired ketene. This will be the subject of a separate publication.<sup>13</sup>

## Conclusion

Previously unknown 2-pyridylketenes **10** are generated by FVT of triazolopyridines **7**. The ketenes dimerise below room temperature to form previously unknown quinolizine-2,4-diones **11** in a [2 + 4]-cycloaddition reaction. FVT of the quinolizinediones causes [2 + 4]-cycloreversion to the ketenes **10**. Photolysis of **7** is a much less efficient route to 2-pyridylketenes.

## Experimental

The equipment used for matrix isolation, preparative FVT and photolysis has been described previously.<sup>1,14</sup>

## Materials

3-Acetyl- and 3-benzoyl-1,2,3-triazolo[1,5-*a*]pyridines **7a,b** were prepared by the method of Regitz.<sup>15</sup>

## FVT of 3-acetyl-1,2,3-triazolo[1,5-*a*]pyridine **7a**

FVT of the triazole **7a** at 700 °C and subsequent FTIR investigation of the Ar matrix isolated pyrolysate indicated the quantitative formation of methyl(2-pyridyl)ketene **10a**;  $\nu_{\text{max}}$  (Ar, 7 K)/ $\text{cm}^{-1}$  2139w, 2132w, 2115vs, 2100s, 1594w, 1588s, 1483w, 1469s, 1431w, 1300w, 1259w, 1153w, 1100w, 1079w, 1046w, 985w and 773m (see Fig 1). On isolation of ketene **10a** in liquid nitrogen [ $\nu_{\text{max}}$  (neat, 77 K)/ $\text{cm}^{-1}$  2106vs, 2093s, 1586s, 1466s, 1257m and 772m] and subsequent warming to room temperature, the IR bands due to **10a** disappeared, and new bands appeared [ $\nu_{\text{max}}$  (neat, 20 °C)/ $\text{cm}^{-1}$  1721s, 1634m, 1614m, 1544s] due to dimerisation to quinolizine **11a**.

### 1,3-Dimethyl-3-(2-pyridyl)quinolizine-2,4(3H)-dione (11a)

A sample of triazole **7a** (200 mg, 1.24 mmol) was thermolysed at 650 °C during 30 min ( $10^{-4}$  mbar). The product was condensed on a cold finger at  $-192$  °C and subsequently allowed to come to room temperature under an Ar atmosphere. The crude product was taken up in dichloromethane, evaporated, and recrystallized from ethyl acetate to yield 152 mg (92%) of crystals; mp 150–152 °C (Found C, 71.92; H, 5.28; N, 10.26.  $C_{16}H_{14}N_2O_2$  requires C, 72.16; H, 5.30; N, 10.52%);  $\nu_{\max}$  (KBr)/ $cm^{-1}$  1728s, 1642m, 1618s, 1554s. The proton NMR spectrum was assigned on the basis of selective spin decoupling experiments, and the  $^1H$  and  $^{13}C$  spectra were correlated by means of HMBC and HSQC pulse sequences; the pyridine ring is numbered C-2'–C-6';  $\delta_H$  ( $CDCl_3$ ) 8.42 (1 H, ddd,  $J$  4.9, 1.9, 1 Hz, 6'-H), 7.96 (1 H, ddd,  $J$  7.5, 1.1, 1 Hz, 6-H), 7.68 (1 H, ddd,  $J$  8.0, 7.5, 1.9 Hz, 4'-H), 7.46 (1 H, ddd,  $J$  8.0, 1.0, 1 Hz, 3'-H), 7.17 (1 H, ddd,  $J$  7.5, 4.8, 1 Hz, 5'-H), 6.82 (1 H, ddd,  $J$  9.5, 5.8, 1 Hz, 8-H), 6.73 (1 H, ddd,  $J$  9.5, 1.0, 1 Hz, 9-H), 6.05 (1 H, ddd,  $J$  7.5, 5.8, 1 Hz, 7-H), 1.87 (3 H, s, 3-Me) and 1.82 (3 H, s, 1-Me);  $\delta_C$  ( $CDCl_3$ ) 190.41 (s, C-2), 175.25 (s, C-4), 160.69 (s, C-2'), 148.87 (d, C-6'), 148.04 (s, C-9a), 137.02 (d, C-4'), 134.00 (d, C-8), 128.15 (d, C-9), 122.55 (d, C-6), 121.73 (d, C-3'), 121.24 (d, C-5'), 108.86 (d, C-7), 101.80 (s, C-1), 63.68 (s, C-3), 21.78 (q, Me-3), 9.34 (q, Me-1);  $m/z$  266 ( $M^+$ , 13%), 238 ( $M^+ - CO$ , 54), 134 (44), 106 (100), 105 (84), 104 (42), 78 (27) and 43 (80).

### FVT of quinolizinedione 11a

FVT of the dimer **11a** at 650 °C and subsequent IR investigation of the Ar matrix isolated thermolysate indicated quantitative formation of methyl(2-pyridyl)ketene **10a**.

### FVT of 3-benzoyl-1,2,3-triazolo[1,5-a]pyridine 7b

FVT of the triazole **7b** at 700 °C and subsequent IR investigation of the Ar matrix isolated pyrolysate indicated the quantitative formation of phenyl(2-pyridyl)ketene **10b**;  $\nu_{\max}$  (Ar, 10 K)/ $cm^{-1}$  2117vs, 1601w, 1590s, 1497m, 1467s, 1455w, 1436m, 1226w, 1308w, 1274m, 1151w, 1127w, 788s, 775m, 767m (for a spectrum, see the supplementary data).

### 1,3-Diphenyl-3-(2-pyridyl)quinolizine-2,4(3H)-dione (11b)

A sample of triazole **7b** (200 mg, mmol) was thermolysed at 700 °C during 30 min ( $10^{-4}$  mbar). The product was condensed on a cold finger at  $-192$  °C and then allowed to come to room temperature under an Ar atmosphere. The crude product was taken up in dichloromethane, evaporated, and recrystallized from ethyl acetate–hexane to yield 140 mg (75%) of fine crystals; mp 188–191 °C (Found C, 80.26; H, 4.77; N, 7.18.  $C_{26}H_{18}N_2O_2$  requires C, 79.98; 4.65; N, 7.18%);  $\nu_{\max}$  (KBr)/ $cm^{-1}$  1744w, 1719s, 1643w, 1626s, 1589w, 1530m, 1551s, 1398m, 1130m, 929m and 702m;  $\lambda_{\max}$  (MeCN) 394 nm. The NMR spectra were assigned on the basis of comparison with the data for **11a**; the pyridine ring is numbered C-2'–C-6'; the benzene rings are numbered C-1''–C-6'';  $\delta_H$  ( $CDCl_3$ ) 8.57 (1 H, ddd,  $J$  6, 2, 2 Hz, 6'-H), 8.02 (1 H, ddd,  $J$  7.7, 1, 1 Hz, 6-H), 7.61 (1 H, ddd,  $J$  7.8, 7.8, 1 Hz, 4'-H), 7.45–7.29 (6 H, m, Ar-H), 7.24–7.17 (5 H, m, Ar-H), 6.99 (1 H, ddd,  $J$  9.0, 1.1, 1 Hz, 9-H), 6.66 (1 H, ddd,  $J$  9.0, 5.8, 1 Hz, 8-H), 6.56 (1 H, ddd,  $J$  9.5, 1.5, 1 Hz, Ar-H), 6.07 (1 H, ddd,  $J$  7.7, 5.8, 1 Hz, 7-H);  $\delta_C$  ( $CDCl_3$ ) 188.33 (s, C-2), 173.62 (s, C-4), 160.61 (s, C-2'), 148.87 (d, C-6'), 139.54 (s, C-9a), 136.46 (d, C-4'), 136.10 (s, C-1''), 134.23 (d, C-8), 129.79 (d, C-9), 128.84 (d), 128.66 (d), 128.53 (d), 127.80 (d), 125.50 (d, C-6), 122.87 (d, C-3'), 122.48 (d, C-5'), 111.06 (s, C-1), 109.92 (d, C-7) and 74.97 (s, C-3);  $m/z$  390 ( $M^+$ , 6%), 364 ( $M^+ - CO$ , 6), 362 (7), 196 (30), 195 (63), 194 (19), 169 (72), 168 (100), 167 (71), 44 (35) and 43 (32).

### FVT of quinolizinedione 11b

FVT of the dimer **11b** at 650 °C and subsequent IR investigation of the thermolysate, isolated at  $-192$  °C, indicated quantitative formation of phenyl(2-pyridyl)ketene **10b**;  $\nu_{\max}$  (neat, 77 K)/ $cm^{-1}$  2117s, 1590m, 1497w, 1466m, 1436m.

### Photolysis of 3-acetyl-1,2,3-triazolo[1,5-a]pyridine (7a)

A matrix isolated sample of **7a** (Ar, 30 K;  $\nu_{\max}$  (Ar, 7 K)/ $cm^{-1}$  1687m, 1678m, 1520s, 1435m, 1420m, 1356m, 1209s, 1054m and 951m) was irradiated with a 1000 W high-pressure Hg/Xe lamp at  $\lambda > 300$  nm (quartz) for 10 min. The IR bands due to **7a** disappeared, and new bands appeared:  $\nu_{\max}$  (Ar, 30 K)/ $cm^{-1}$  2139vw, 2116s, 2100m, 1794w, 1747m, 1593m, 1537m, 1404m and 1013m.

### Photolysis of 3-benzoyl-1,2,3-triazolo[1,5-a]pyridine (7b)

A matrix isolated sample of **7b** ( $\nu_{\max}$  (Ar, 7 K)/ $cm^{-1}$  3084w, 1645m, 1520m, 1514s, 1426m, 1412m, 1271m, 1258m, 1228m, 1093m, 936m and 883m) was irradiated at 28 K as above using  $\lambda > 320$  nm or  $\lambda > 345$  nm (cut-off filters). The IR bands due to **7b** disappeared and new bands appeared:  $\nu_{\max}$  (Ar, 30 K)/ $cm^{-1}$  2110w, 1770s, 1515vs, 1365m, 940s, 621w. The species absorbing at 1770  $cm^{-1}$  appeared faster than the ketene absorbing at 2110  $cm^{-1}$ .

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