Mesoions and ketene valence isomers. Three types of rearrangement of mesoionic pyridopyrimidinylium olates involving ketene intermediates †

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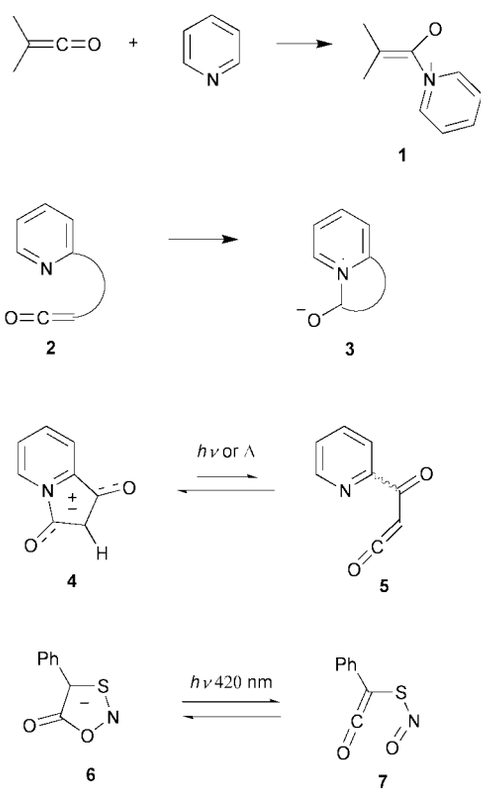
The ketene valence isomers of mesoionic pyrimidinylium olates undergo (i) a retro-ene type fragmentation to C_3O_2 **16** and 2-aminopyridine **15**, (ii) an electrocyclisation to form a naphthyridine (**19**→**20**→**21**), or (iii) a cycloreversion to 2-pyridyl isocyanate **26** and a ketene **25**.

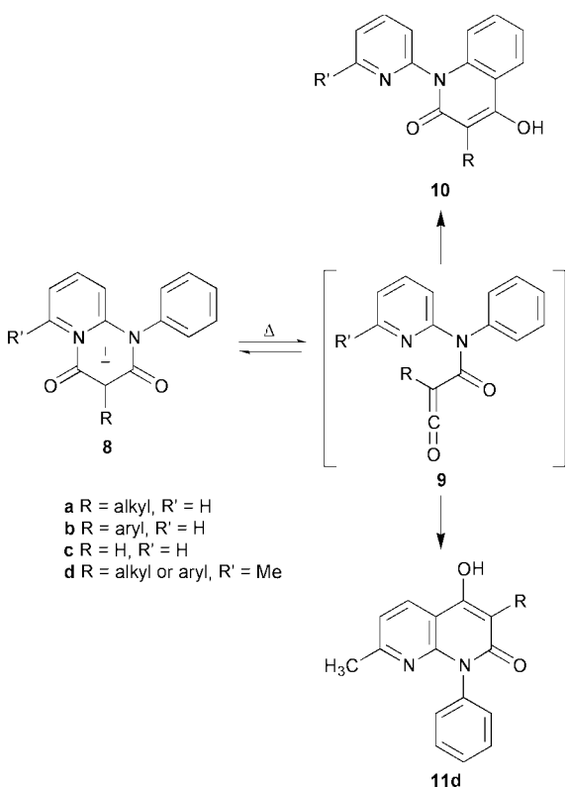
Introduction

Ketenes react with nucleophiles such as pyridine at extremely low temperatures (as low as 15 K) to form zwitterions **1**. These



are normally fleeting species that can only be detected at low temperatures and dissociate easily into the ketene and pyridine constituents.[1] When such a reaction takes place intramolecularly, the outcome is a cyclic zwitterionic (mesoionic) compound (**2**→**3**), which is usually far more stable thermodynamically than the open-chain ketene.[2] Although there has been much speculation in the literature on the ring opening of both five-membered (sydnones and münchnones) and six-membered mesoionic heterocycles to the isomeric ketenes,[3] there are in fact only two well-established cases, *viz*. that of the pyrrolo[1,2-*a*]pyridinylium olate (**4**→**5**)[2] and that of 1,3,2-oxathiazolylium-5-olate (**6**→**7**).[4]

The first rearrangement of the six-membered pyridopyrimidinylium olates was discovered by Kappe and Lube. On heating in the condensed phase, 1-phenylpyridopyrimidinylium olates **8** rearrange to quinolones **10**, presumably *via* electrocyclisation of the unobserved ketenes **9** onto the adjacent phenyl ring, a reaction which can also be regarded as an electrophilic aromatic substitution by the ketene (Scheme 1).[5]



Scheme 1

Since the electron density in benzene is higher than that in pyridine, the ketene does not usually undergo the alternative cyclisation to afford a naphthyridine **11**, but this pathway takes place in the 6-methyl derivatives **8d**.[6] Analogous results with

† Four argon matrix infrared spectra corresponding to Fig. 1 are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/b0/b003662p

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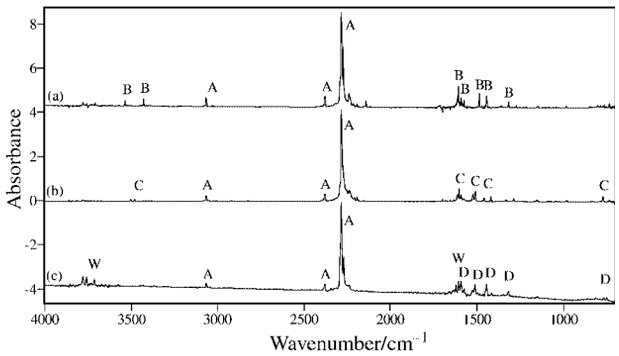


Fig 1 FTIR spectra (Ar matrix, 12 K) of the products of FVT at 720 °C of the pyrimidinylium olates **12a–c** (a–c). Bands are labelled A (C_3O_2, **16**, 3065, 2380, 2286, 2272 cm^{-1}), B (2-aminopyridine **15a**), C (2-methylaminopyridine **15b**), D (2-anilinopyridine **15c**) and W (water). These spectra are reduced by a factor 5. Actual absorbance values for the strongest C_3O_2 peak are 1.5 (a), 4 (b), and 0.6 (c). The full scale spectra are available as Electronic Supporting Information.

solution phase thermolysis of mesoionic pyrimidopyridazinylium olates, giving both quinolones and pyridopyridazinones as products have been reported.[7]

We have recently investigated the structures of six-membered mesoionic pyridopyrimidinylium and pyridooxazinylium olates.[3] Here we describe the results of experiments aimed at detecting the ring opening of these compounds to the isomeric ketenes. We have found that three types of thermal rearrangement *via* ketene intermediates can take place.

Results and discussion

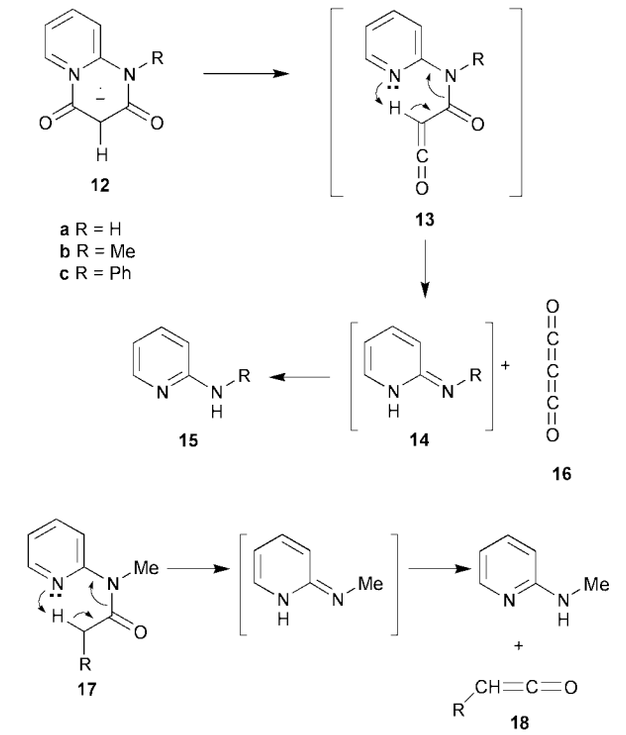
1. FVT of 3-unsubstituted pyrimidinium olates (12a–c). C_3O_2 formation

Flash vacuum thermolysis (FVT) of compounds **12** at 700 °C caused fragmentation to carbon suboxide C_3O_2 (**16**)[8] and the corresponding substituted 2-aminopyridine **15**. These compounds were rigorously identified by comparison of the Ar matrix IR spectra with those of authentic materials (Fig. 1). Larger scale IR spectra are presented in the Electronic Supporting Information.† The reactions presumably proceed *via* the oxoketene intermediate **13** and the 2-iminopyridine **14** and is analogous to the fragmentation of *N*-(2-pyridyl)amides to ketenes reported previously[9] (**17**→**18**) (Scheme 2). Both of these reactions can be regarded as pseudo-pericyclic retro-ene type processes—pseudopericyclic because the nitrogen lone pair is likely to be involved.[10]

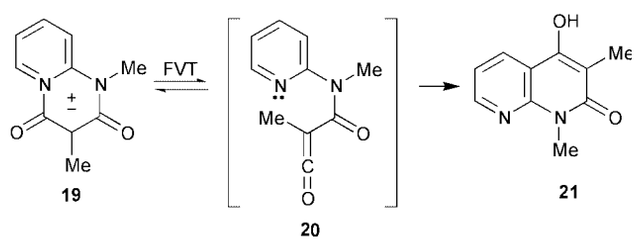
The fragmentation of compounds **12b**,**c** proceeded cleanly in the temperature range 360–700 °C. In contrast, the unsubstituted compound **12a** underwent no significant conversion until 500 °C, when C_3O_2 and 2-aminopyridine became the major products. The results at 720 °C are shown in Fig. 1c and elaborated again in section 3. The ketene intermediates **13** could not be observed directly in any of these thermolyses. As mentioned in the introduction, olate **12c** (= **8c**) behaved differently on thermolysis in the solid state, rearranging to the quinolone **10**.[5]

2. FVT of the 3-methylpyrimidinylium olate 19. Rearrangement to naphthyridone 21

In order to avoid the H-shift which occurred in compounds **12** and resulted in clean C_3O_2 formation, we prepared the 1,3-dimethyl olate **19**.[3] When **19** was subjected to preparative FVT at 700 °C, the naphthyridone **21** was obtained in 65% isolated yield (Scheme 3). The naphthyridone is formed in this case because the 1-phenyl group in **8/9** is missing; hence the oxoketene intermediate **20** has no alternative but to revert to the starting material **19** or cyclise at the 3-position of pyridine, giving **21**.



Scheme 2



Scheme 3

The same FVT reaction was investigated under Ar matrix isolation conditions. At temperatures above 600 °C the formation of a ketene was observed (2129 cm^{-1}) in addition to unchanged starting material **19** and the naphthyridone **21**. The ketene may or may not be compound **20**. In spite of the presence of the 3-methyl group, some rearrangement with C_3O_2 formation takes place in this compound too: an increase of the pyrolysis temperature (T > 650 °C) yielded new IR bands indicating the formation of small amounts of C_3O_2 (**16**, 2286 and 2272 cm^{-1}). Neither 2-(dimethylamino)pyridine nor 1-methyl-2-(methylimino)pyridine were identifiable in the IR spectra by comparison with authentic samples.

3. Fragmentation to 2-pyridyl isocyanate and ketenes

N(1)-Unsubstituted pyridopyrimidinones **22** can undergo one further type of fragmentation, namely a cycloreversion to afford 2-pyridyl isocyanate **26** and a ketene **25** (Scheme 4). This is most easily explained as a cycloreversion in the otherwise unobserved, least favoured tautomer **24**. It is known from our previous work that the *OH*-tautomers **23** are energetically preferred over the mesoions **22** in the gas phase, and hence **23** is observed in the Ar matrix spectra.[3] The *CH*-tautomers **24** are calculated to lie some 13 kcal mol^{-1} above **22** in the gas phase and are therefore readily accessible under high temperature FVT conditions.[3]

Thus, FVT of **22b** above 500 °C with matrix isolation of the products in Ar at 10 K afforded 2-pyridyl isocyanate **26** and methylketene **25b** (Fig. 2a). The proof for the formation of isocyanate **26** was provided by independent generation and matrix isolation of this material. The acyl azide **27** is an

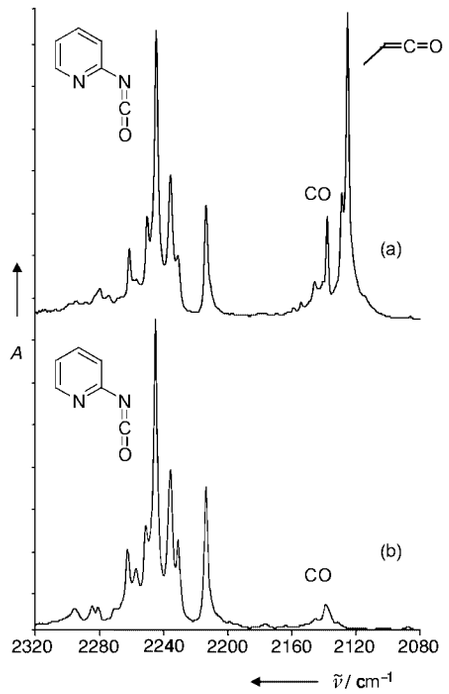
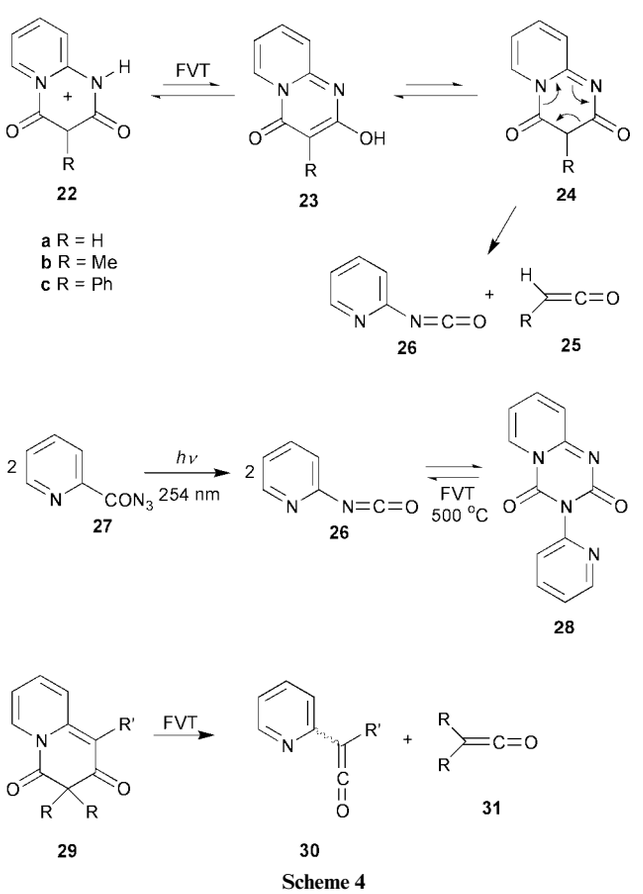


Fig. 2 FTIR spectra (Ar matrix, 10 K) of 2-pyridyl isocyanate **26** obtained by (a) FVT of **22b** at 800 °C with concomitant formation of methylketene **25b** (2125 cm^{-1}), (b) matrix photolysis of **27** at 254 nm.



Scheme 4

unstable compound which easily undergoes the Curtius rearrangement with dimerisation to **28** in solution.[11] Deposition of **27** by gentle vaporisation at 13 °C in a stream or Ar with matrix deposition at 10 K and subsequent irradiation at 254 nm afforded the isocyanate **26**, whose complex IR spectrum is identical with the one obtained from **22b** (Fig. 2). The same IR spectrum of **26** was also obtained by FVT of the dimer **28** at 500 °C. The cycloreversion of **24** is analogous to that of **28**, and also to that of the novel quinolizinediones **29** to ketenes **30** and **31** recently reported by us.[12]

The presence of methylketene **25b** in the thermolysate from **22** (Fig. 2, strongest band at 2125 cm^{-1}) was proved by comparison with previously recorded matrix spectra.[13] This reaction pathway, to **25** and **26**, occurred throughout the temperature range 500–950 °C.

Similarly, the 3-phenyl derivative **22c** also afforded **26** and phenylketene[14] **25c** (2121 cm^{-1}) on FVT at 600 °C, less quantitatively in this case because of the low volatility of **22c**. Even in the case of the unsubstituted compound **22a** (= **12a**) the fragmentation according to Scheme 4 competes with the C_3O_2 formation according to Scheme 2. While the main product is C_3O_2 (peaks A in Fig. 1a), small peaks due to 2-pyridyl isocyanate **26** are seen at 2213–2244 cm^{-1}, and a peak due to ketene **25a**[15] appears at 2142 cm^{-1}. A larger-scale spectrum showing these details is available as Electronic Supporting Information.†

Conclusions

Depending on the substituent pattern, the ketene valence isomers generated by FVT of pyrimidinylium olates undergo three types of rearrangement, *viz*. ring transformations to form quinolines or naphthyridines (Schemes 1 and 3), a retro-ene type fragmentation to C_3O_2 (Scheme 2), or a cycloreversion to 2-pyridyl isocyanate and a ketene (Scheme 4). The placement of substituents in position 3 of the starting material hinders the fragmentation to C_3O_2 so that reaction according to either Scheme 3 or Scheme 4 will occur. The presence of the *N*(1)-H function allows tautomerisation to **24** and makes fragmentation to 2-pyridyl isocyanate and a ketene preferred (Scheme 4). When also this reaction pathway is blocked by an *N*(1) substituent, cyclisation to a naphthyridone or quinolone (Schemes 1 and 3) takes place.

Experimental

General details

Infrared spectra were recorded on a Perkin-Elmer 1700X or System 2000 FT-IR spectrometer. UV spectra were measured on a Shimadzu UV-1601 spectrometer. Mass spectra were obtained using a Kratos MS25RFA spectrometer (EI, 70 eV). NMR spectra were recorded on a Bruker AC 200 spectrometer (200 MHz for ^1H and 50 MHz for ^{13}C) in $CDCl_3$ or D_6-DMSO with $SiMe_4$ as internal standard. *J* values are given in Hz. Preparative FVT experiments were performed using electrically heated quartz tubes (length 40 cm, diameter 2 cm). Samples were sublimed into the pyrolysis tube using a Büchi sublimation oven. The system was evacuated to approximately 10^{-4} mbar and continuously pumped during the pyrolysis using a Leybold–Heraeus turbomolecular pump, PT150. The pyrolysis products were trapped on a cold finger at liquid N_2 temperature.

Matrix isolation experiments were carried out using Leybold–Heraeus ROK 10-300 or Air Products CSW-202-6.5 closed cycle He cryostats with BaF_2 or KBr windows, the latter equipped with a Lakeshore Model 330 temperature controller. All compounds were directly sublimed onto the cold window at 7–30 K, and simultaneously a large excess of Ar (99.999%, BOC Gases Australia Ltd) was deposited. In FVT experiments a mixture of Ar and sample was led through a quartz tube (10 cm length, 0.8 cm diameter) equipped with a heating wire and a thermocouple and subsequently trapped on the cold window.[16] Thin film depositions at 77 K were carried out on an Air Products liquid N_2 cryostat using methodology similar to that for the matrix isolation experiments.

Materials

The pyridopyrimidinylium olates were prepared according to

ref. 3 and literature procedures therein, **12b** according to ref. 17 and **12c** according to ref. 18.

FVT of 2-oxo-1,2,3,4-tetrahydropyrido[1,2-*a*]pyrimidin-5-ium-4-olate 12a

FVT at 720 °C and subsequent IR investigation of the matrix isolated product illustrates the formation of C_3O_2 [**16**; ν_{max}(Ar, 12 K)/cm^{-1} 3065w, 2380w, 2286vs and 2272s] and 2-aminopyridine [**15a**; ν_{max}(Ar, 12 K)/cm^{-1} 3535vw, 3430vw, 1611w, 1608w, 1575w, 1483w, 1445w and 1316w, identical with that of an authentic sample] as main products. In addition, minor unidentified bands at 2386w, 2245m, 2240m and 2142w cm^{-1} were obtained. FVT in the range 500–650 °C gave a mixture of the starting material **12a** and the fragmentation products **15a** and **16**.

FVT of 1-methyl-2-oxo-1,2,3,4-tetrahydropyrido[1,2-*a*]-pyrimidin-5-ium-4-olate 12b

FVT in a range of 360–720 °C and subsequent IR investigation of the matrix isolated product demonstrated the formation of C_3O_2 [**16**; ν_{max}(Ar, 12 K)/cm^{-1} 3065w, 2380w, 2286vs and 2272s] and 2-(methylamino)pyridine [**15b**; ν_{max}(Ar, 12 K)/cm^{-1} 3504vw, 3480vw, 1617w, 1611w, 1524w, 1510w, 1459w, 1421w, 1156vw and 771w, identical with that of an authentic sample] as the near-exclusive products, together with very weak unassigned peaks at 2194 and 2208 cm^{-1}.

FVT of 1-phenyl-2-oxo-1,2,3,4-tetrahydropyrido[1,2-*a*]-pyrimidin-5-ium-4-olate 12c

FVT in a range of 360–720 °C and subsequent IR investigation of the matrix isolated product demonstrated the formation of C_3O_2 [**16**; ν_{max}(Ar, 12 K)/cm^{-1} 3065w, 2380w, 2286vs and 2272s] and 2-anilinopyridine [**15c**; ν_{max}(Ar, 12 K)/cm^{-1} 3438w, 1609m, 1595m, 1575m, 1526w, 1514m, 1486w, 1447m and 1318w] as the near-exclusive products. An authentic sample of **15c** was prepared according to the literature.[19] Compound **12c** itself had the following matrix IR spectrum: ν_{max}(Ar, 28 K)/cm^{-1} 1740s, 1700s, 1676m, 1513m, 1496w, 1355w, 1306m, 1235m, 1227m, 773w and 727w. The IR spectrum of **12c** in KBr has been reported.[17]

FVT of 1,3-dimethyl-2-oxo-1,2,3,4-tetrahydropyrido[1,2-*a*]-pyrimidin-5-ium-4-olate 19

FVT at 830 °C and subsequent IR investigation of the Ar matrix isolated product revealed the formation of a ketene [new bands in the spectrum, not necessarily all due to the same compound, at ν_{max}(Ar, 12 K)/cm^{-1} 2154w, 2129s, 2113w, 1684m, 1571m, 1490s, 1444m, 1318m and 771m]. A significant amount of the naphthyridine **21** was formed according to bands at 3603m, 1666m, 1655s, 1472m, 985w and 779w cm^{-1}. A band due to C_3O_2 was observed at 2275 cm^{-1}. No bands due to 2-(dimethylamino)pyridine[20] [ν_{max}(Ar, 28 K)/cm^{-1} 1610m, 1601s, 1513m, 1426m, 1375w, 983w and 769w] or 1-methyl-2-(methylimino)pyridine[19] [ν_{max}(Ar, 28 K)/cm^{-1} 1660s, 1649m, 1595s, 1407m, 1341m, 1062m, 1047m, 768m and 734m] were identifiable.

4-Hydroxy-1,3-dimethyl-1,8-naphthyridin-2(1*H*)-one 21

The olate **19** (300 mg, 1.6 mmol) was thermolysed at 700 °C during 1 h (10^{-4} mbar). The products were condensed on a cold finger at −192 °C and allowed to warm up to room temperature. The crude product was washed with acetone and recrystallized from acetone to yield 195 mg (65%) of ivory coloured crystals, mp 238–240 °C; ν_{max}(KBr)/cm^{-1} 1639s, 1612s, 1586s, 1489w, 1236m, 1178m, 776m and 459m; ν_{max}(Ar, 14 K)/cm^{-1} 3603s, 1666s, 1658vs, 1595ms, 1524w, 1490w, 1472m, 1315m, 1298w, 1237m, 1222m, 1162m, 1117m, 1095w, 985w, 905w and 779w; λ_{max}(MeCN)/nm 231 (log ε/dm^3 mol^{-1} cm^{-1} 4.122), 248 (4.016), 285 (3.884), 321 (4.117) and 334 (3.944); δ_H(DMSO-d_6) 9.93 (1 H, s, OH), 8.58 (1 H, dd, ^3J 4.7, ^4J 1.7, 7-H), 8.29 (1 H, dd, ^3J 7.8, ^4J 1.7, 5-H), 7.28 (1 H, dd, $^3J_1$ 7.8, $^3J_2$ 4.7, 6-H), 3.65 (3 H, s, N-Me), 2.06 (3 H, s, C-Me); δ_C(DMSO-d_6) 163.67 (s, C-2 or C-4), 154.90 (s, C-2 or C-4), 149.15 (d, C-7), 148.06 (s, C-8), 131.51 (d, C-5), 117.40 (d, C-6), 111.74 (s, C-4a), 107.22 (s, C-3), 27.92 (q, N-Me), 9.99 (q, C-Me); *m*/*z* 191 (12%), 190 (M^+, 100), 162 (29), 161 (24), 147 (23) and 91 (13); Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.36; H, 5.25; N, 14.62%.

Pyridine-2-carbonyl azide 27

This compound was prepared according to the literature[20] and stored in the freezer as a benzene solution (*ca*. 1 g 10 ml^{-1}). IR (neat film)/cm^{-1} 2190 (w), 2138 (s), 1697 (s), 1584 (w), 1438 (w), 1302 (w), 1283 (s), 1241 (s), 1181 (s), 1010 (s), 745 (m), 708 (m), 688 (m); IR (Ar matrix), see below under matrix isolation of **25**.

3-(2-Pyridyl)-2,3,4,5-tetrahydropyrido[1,2-*a*][1,3,5]triazine-2,4-dione 28

This compound was prepared according to the literature;[11c] mp 222–226 °C (lit.[11e] 228–230 °C, lit.[11c] 243–245 °C); δ_H(DMSO-d_6) 7.0 (dd, 1 H, 7-H), 7.17 (d, 1 H, 9-H), 7.54 (m, 2 H, 2′,4′-H), 7.91 (dd, 1 H, 8-H), 8.04 (dt, 1 H, 3′-H), 8.44 (d, 1 H, 6-H), 8.61 (d, 1 H, 6′-H); δ_C(DMSO-d_6) 114.7, 124.4, 125.1, 125.9, 130.6, 140.4, 144.0, 149.6, 150.4, 150.7, 153.8, 155.9; IR (KBr)/cm^{-1} 1749 (m), 1701 (s), 1651 (s), 1560 (s), 1550 (s), 1469 (w), 1375 (m), 1276 (m), 766 (m); MS [*m*/*z* (% rel. int.)]: 240 (*M*, 4), 198 (3), 121 (33), 120 (100), 92 (14), 78 (8); UV (1,4-dioxane), λ_{max}/nm 214 (13300), 256 (14300), 264 (12600), 340 (4300), 354 (4700), 375 (2300); fluorescence (0.4 mmol 10 ml^{-1} 1,4-dioxane), λ_{ex}/nm (int) 308 (83), 378 (87); λ_{em}/nm (int) 408 (44); 430 (44); Anal. Calcd for $C_{12}H_8N_4O_2$: C, 60.00; H, 3.36; N, 23.32. Found: C, 59.89; H, 3.70; N, 23.45%.

2-Pyridyl isocyanate 26

Method A. Matrix isolation and photolysis of pyridine-2-carbonyl azide 27. The azide **27** was sublimed at 13 °C and deposited with Ar at 7 K. The azide was characterised by IR (Ar matrix, 7 K)/cm^{-1}: 2203 (w), 2138 (s), 1701 (m), 1285 (s), 1244 (m), 1190 (s), 1013 (m). The matrix isolated azide was irradiated at 254 nm for 25 min, and the resulting 2-pyridyl isocyanate **26** was characterised by IR (Ar matrix, 7 K; see Fig. 2)/cm^{-1}: 2262 (w), 2257 (w), 2251 (w), 2245 (s), 2236 (m), 2231 (w), 2213 (m), 1594 (m), 1477 (w), 1151 (w), 777 (w).

Method B. FVT of 2-pyridyl isocyanate dimer 28. 3-(2-Pyridyl)-2,3,4,5-tetrahydropyrido[1,2-*a*][1,3,5]triazine-2,4-dione **28** was sublimed (110 °C) and pyrolysed (500 °C) with Ar matrix deposition at 7 K. The product was identified as 2-pyridyl isocyanate **26** by identity with the spectrum shown in Fig. 2b.

Acknowledgements

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