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Full Paper

Ketenes from *N*-(2-Pyridyl)amides

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Methoxycarbonylketene **4a**, methoxycarbonyl(methyl)ketene **4b**, chloroketene **4c**, cyanoketene **4d**, diphenylketene **4e**, and 2-pyridylketene **4f** have been generated by flash vacuum thermolysis of the corresponding 2-pyridylacetamide derivatives **3a**–**f** and isolated in Ar matrices for FT-IR spectroscopic characterisation. The *N*-(2-pyridyl)-2-pyridylacetamide **3f** yielded 2-pyridyl isocyanate in addition to 2-pyridylketene.

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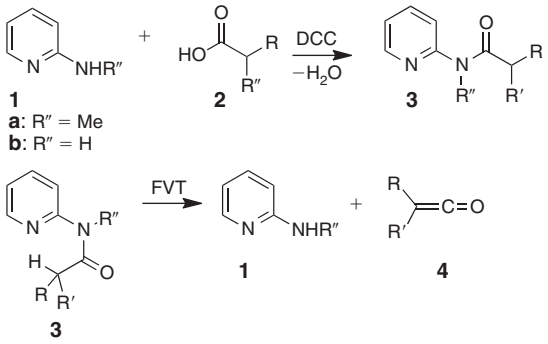
Introduction

While there are many methods for the synthesis of ketenes,[1] we were interested in developing a procedure that would help us identify ketenes formed in either thermal or photochemical reactions and isolated in low temperature noble gas matrices. For this purpose, an efficient method amenable to flash vacuum thermolysis (FVT) with Ar matrix isolation of the products and capable of being applied to a wide variety of ketenes was desirable. In a preliminary publication we reported the formation of methoxycarbonylketene **4a** by FVT of the 2-pyridylacetamide derivative **3a**.[2] We have now examined the scope of this reaction by generating the ketenes **4a**–**f** and are pleased to report the details herein.

Results and Discussion

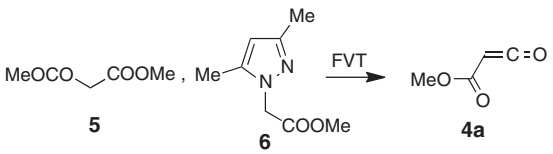
The requisite *N*-(2-pyridyl)acetamides **3** were prepared by condensation of *N*-methyl-*N*-(2-pyridyl)amine **1a** or 2-pyridylamine **1b** with acetic or malonic acid derivatives **2** by using dicyclohexylcarbodiimide (DCC) as a dehydrating agent (Scheme 1). Ketenes **4** were generated by FVT of **3** in high vacuum and condensed with Ar at 10–15 K to form a matrix. The reaction is a retro-ene type cycloelimination. The IR spectrum of methoxycarbonylketene **4a** obtained in this manner at 480°C is shown in Fig. 1.

The identity of compound **4a** was confirmed by comparison with the spectra obtained by FVT of two other precursors, viz. dimethyl malonate **5** and 3,5-dimethyl-*N*-(methoxycarbonylacetyl)pyrazole **6** (Eqn 1). As described previously,[2] the same ketene was obtained by all three methods, but the pyridylamide route from **3a** afforded the cleanest spectrum. The strong C=C=O stretch of **4a** is at 2156 cm^{-1}. At 480°C a small amount of carbon suboxide, C_3O_2, was the only noticeable by-product (C, Fig. 1), but this increased at higher temperatures. Formation of C_3O_2 was more of a problem in the FVT of dimethyl malonate **5**, and the hygroscopic nature



Scheme 1. Synthesis of *N*-(2-pyridyl)amides **3** and ketenes **4**. Yields of **3** given in percent.

and incomplete pyrolysis of the pyrazole derivative **6** made this a less useful precursor.



(1)

The methyl 2-methylmalonic amide derivative **3b** underwent analogous FVT at 480°C yielding a very clean Ar matrix of methoxycarbonyl(methyl)ketene **4b** with its main IR absorption

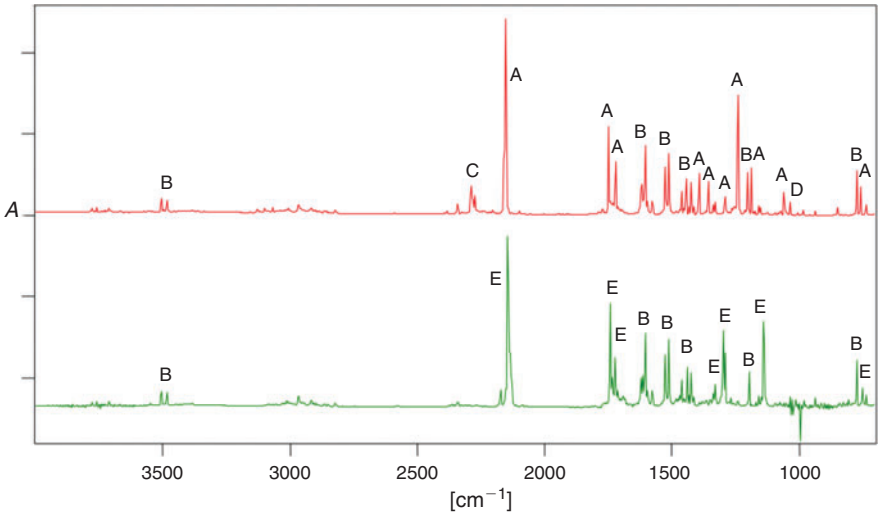


Fig. 1. IR spectra (Ar, 14 K) of methoxycarbonylketene **4a** (top) and methoxycarbonyl(methyl)ketene **4b** (bottom) obtained by thermolysis of **3a** and **3b**, respectively, at 480°C. A: Ketene **4a**; B: Amine **1a**; C: C_3O_2 (3065 (w), 2380 (w), 2286 (vs) and 2272 (s) cm^{-1}) D: MeOH; E: Ketene **4b**. Ordinate: absorbance in arbitrary units.

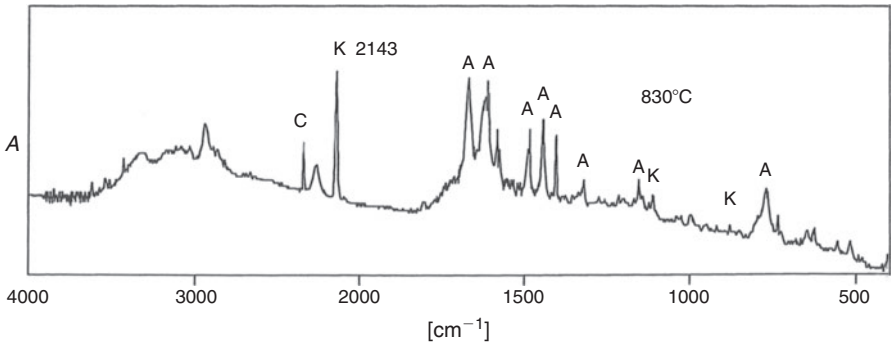


Fig. 2. IR spectrum (Ar, 10 K) of chloroketene **4c** formed by FVT of **3c** at 830°C. K = ketene **4c**, A = 2-aminopyridine, C = CO_2. Ordinate: absorbance.

at 2144 cm^{-1}. No C_3O_2 or other by-products were noticeable in this case (Fig. 1). In the above experiments *N*-methyl-*N*-(2-pyridyl)amine **1a** was used as a starting material and hence also as a leaving group. However, this is not necessary; 2-pyridylamine **1b** is equally good, and this was used in the following experiments.

Chloroketene **4c** was obtained by FVT of **3c** above 790°C. In this case, very little decomposition took place at lower FVT temperatures. The best yield of ketene was obtained at 830°C. The Ar matrix IR spectrum is shown in Fig. 2, where the main C=C=O absorption is seen at 2143 cm^{-1}. The spectrum is in good agreement with the spectrum obtained by photolysis of chloroacetyl chloride in a Xe matrix.[3]

Cyanoketene **4d** was obtained by FVT of **3d** at 775°C (Fig. 3). The CN group appears as a relatively weak absorption at 2239 cm^{-1}, and the very strong ketene stretch at 2163 cm^{-1}.[4]

Diphenylketene **4e** was obtained by FVT of the diphenylacetamide derivative **3e** at 600°C. The Ar matrix IR spectrum (Fig. 4) shows the very strong C=C=O absorption at 2106 cm^{-1}. Peaks due to 2-aminopyridine are also noticeable. The identity of the ketene was ascertained by comparison with the IR spectrum of **4e** prepared by other methods.[5,6] Diphenylketene was the first ketene ever to be characterised.[7]

2-Pyridylketene **4f** and 2-pyridyl isocyanate **7** were obtained by FVT of **3f** at 640°C and yielded an IR spectrum featuring two main absorptions in the cumulene region, viz. 2-pyridylketene (2132 cm^{-1}) and 2-pyridyl isocyanate (2257 cm^{-1}) (Fig. 5). We have investigated these two compounds before and therefore were able to identify them securely in the IR spectrum.[6,8,9] An expansion of the ketene region reveals the presence of the two *s-Z* and *s-E* conformers of 2-pyridylketene at 2132 and 2123 cm^{-1} respectively (Fig. S1, Supplementary Material) in exact agreement with the previously reported data for this ketene obtained by the Wolff rearrangement of 2-(diazoacetyl) pyridine.[9]

Isocyanates exhibit very strong and often complex absorptions in the 2200 cm^{-1} region. This is shown for isocyanate **7** in Fig. 6, where excellent agreement with the spectrum obtained by matrix photolysis of 2-picolinyl azide[8] is seen. The formation of both **4f** and **7** in this reaction is obviously due to the presence of two pyridine rings. Thus, two different retro-ene type reactions are possible, as illustrated in Scheme 2. By slow warming of an Ar matrix it is possible to evaporate the Ar and still maintain a solid film for IR observation. This causes broadening of the peaks and shifts towards smaller wavenumbers (Fig. S2, Supplementary Material). When such a warming experiment was performed on the matrix corresponding to the IR spectrum shown in Fig. 4, the ketene was seen to start disappearing at a temperature of 135 K, whereas the isocyanate remained stable till room temperature. The NCO stretching vibrations in

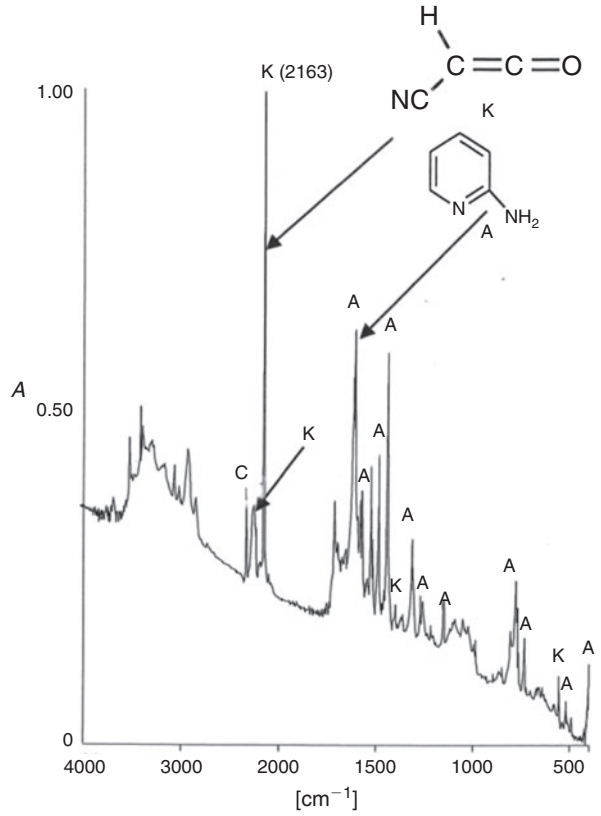


Fig. 3. IR spectrum (Ar, 10 K) of cyanoketene **4d** formed by FVT of **3d** at 775°C. K = ketene **4d**, A = 2-aminopyridine, C = CO_2. Ordinate: absorbance in arbitrary units.

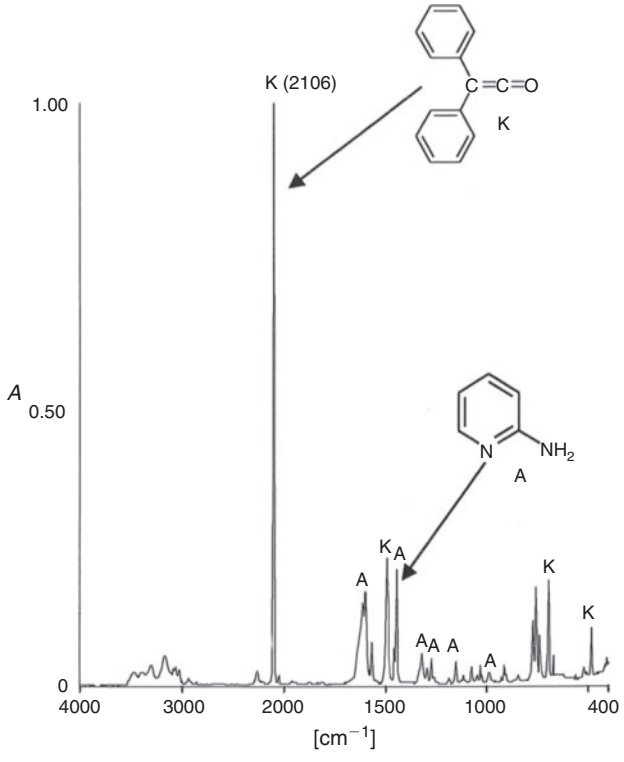


Fig. 4. IR spectrum (Ar, 20 K) of diphenylketene **4e** formed by FVT of **3e** at 600°C. K = ketene **4e**, A = 2-aminopyridine. Ordinate: absorbance in arbitrary units.

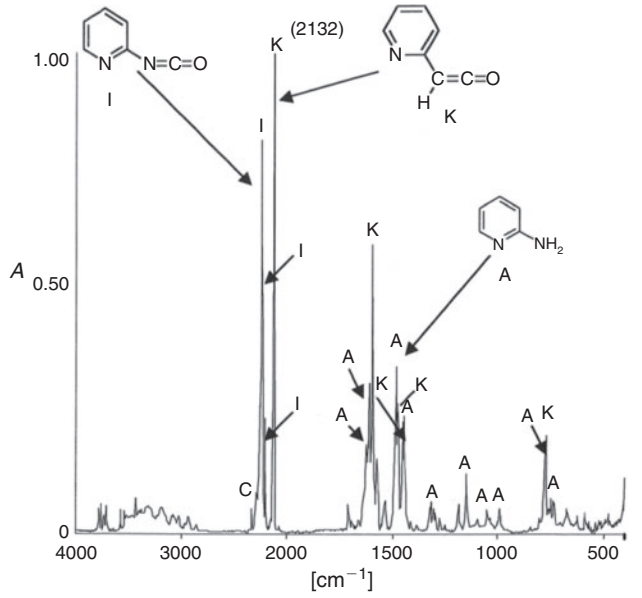


Fig. 5. IR spectrum of 2-pyridylketene **4f** and 2-pyridyl isocyanate **7** (Ar, 10 K) obtained by FVT of **3f** at 640°C. K = ketene **4f**, I = isocyanate **7**. A = 2-aminopyridine, C = CO_2. Ordinate: absorbance in arbitrary units.

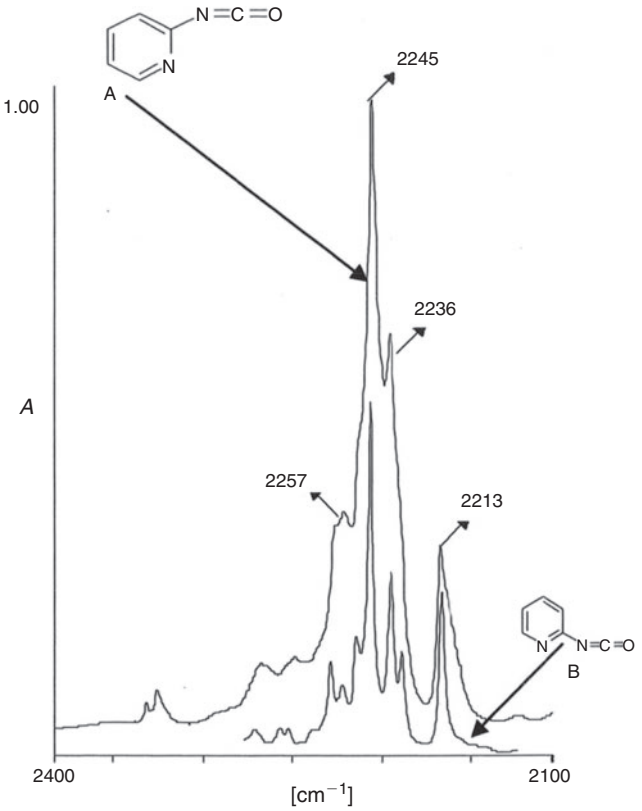
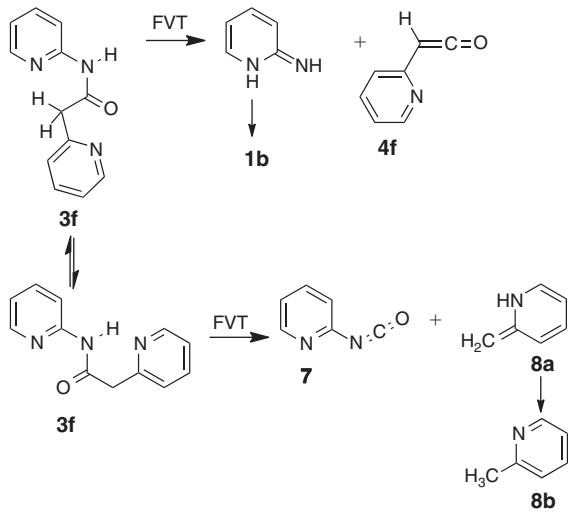


Fig. 6. IR spectrum of 2-pyridyl isocyanate **7** obtained by FVT of **3f** (A) and by Curtius rearrangement of 2-picolinoyl azide[9] (B). Ordinate: absorbance in arbitrary units.

isocyanates are stronger than the C=C=O vibrations in ketenes; i.e. the amount of isocyanate **7** formed is much lower than that of ketene **4f**. When the FVT of **3f** was carried out at 620°C instead of 640°C, the intensity of the isocyanate peak at 2245 cm^{-1} was only ~40 % of that of the ketene at 2133 cm^{-1}.



Scheme 2. Formation of 2-pyridylketene **4f** and 2-pyridyl isocyanate **7**.

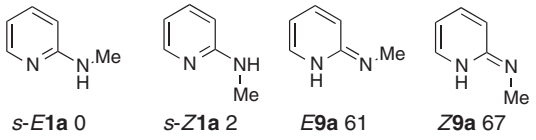


Chart 1. Relative energies of 2-(methylamino)pyridines **1a** and 2-(methylimino)-1*H*-pyridines **9a** in kJ mol^{-1} calculated at the B3LYP/6–311+G**//B3LYP/6–31G* level.

In all the FVT reactions reported here, 2-pyridylamine **1b**, *N*-methyl-*N*-(2-pyridyl)amine **1a**, and 2-picoline **8b** were obtained rather than the corresponding 2-methylene-1*H*-pyridines **8a** (see Scheme 2) or 2-imino-1*H*-pyridines **9** (see Chart 1), which are expected as the initial products of a retro-ene type reaction.

This is ascribed to facile tautomerisation, taking place already in the FVT reactions, possibly during collisions with the hot quartz wall of the pyrolysis tube. It is a common observation that very facile tautomerisation of OH and NH functions can take place under FVT conditions.[10] The aromatic 2-amino-, 2-(methylamino)-, and 2-methylpyridines have significantly lower energies than the corresponding 2-(1*H*)-imine and 2-(1*H*)-methylene derivatives.[11] Our own calculations at the B3LYP/6–311+G**//B3LYP/6–31G* level yield the following relative energies in the gas-phase for 2-(pyridylamino) pyridine **1a**: *s*-*E***1a** (0), *s*-*Z***1a** (2), *E*-2-(methylimino)-1*H*-pyridine *E***9a** (61), and *Z*-2-(methylimino)-1*H*-pyridine *Z***9a** (67 kJ mol^{-1}) (Chart 1). The presence of two NH stretching bands at 3504 and 3480 cm^{-1} in the matrix IR spectrum of **1a** formed in the FVT reaction (Fig. 1) indicates the presence of the two rotameric forms, *s*-*Z***1a** and *s*-*E***1a** respectively. These absorptions have calculated intensities of 20 and 34 kJ mol^{-1}, respectively, at the B3LYP/6–31G* level. Experimentally, the two bands have nearly equal intensities, which means that the *s*-*Z* conformer is in fact the major constituent, and this can be ascribed to lone pair–lone pair repulsion in the *E* isomer. The strongest bands in the 2-(methylimino)-1*H*-pyridine **9a** are calculated at 1667 (*s*-*E*) and 1659 (*s*-*Z*) cm^{-1} (intensities 506 and 377 kJ mol^{-1}, respectively) at the B3LYP/6–31G* level. Weak bands at 1661 cm^{-1} are present in some of the experimental IR spectra (see Fig. S4, Supplementary Material), thereby suggesting that minor amounts of the imine tautomers may be present. It is anticipated that pulsed pyrolysis[10] with supersonic free-jet cooling of the initial pyrolysis products would be the method of choice for the matrix isolation and detection of the unstable iminopyridine tautomers.

Conclusion

FVT of *N*-(2-pyridyl)amides is a versatile method for the synthesis of a variety of ketenes, inter alia alkoxycarbonylketenes, chloroketene, cyanoketene, 2-pyridylketene, and arylketenes. It is emphasised that, apart from diphenylketene, these ketenes are highly reactive species that cannot be isolated under conventional reaction conditions. This method is expected to be applicable in the investigation of many other reactive ketenes.

Experimental

The apparatus and methods used for FVT and matrix isolation have been described in detail.[10] An apparatus analogous to the one illustrated in fig. 7 in ref. [10] was used with an APD HC-2 liquid helium cryostat capable of reaching an ultimate temperature of 7 K. Vacuum was maintained at 10^{-7}–10^{-5} hPa with a Balzers Pfeiffer turbomolecular pump. Starting materials were sublimed into the pyrolysis tube at a temperature of ~75°C, pyrolyses were carried out at the temperatures given in the text, and pyrolysis products were condensed on a CsI target at ~10 K together with Ar in a ratio of roughly 1 : 1000. Gas chromatography–mass spectrometry (GC-MS) was performed on a Hewlett–Packard GC 5890–MS5970 instrument with helium carrier gas, injector port 200°C, initial temperature 100°C, increasing at 16°C per min on a 30-m ALLTECH capillary column. Mass spectra were recorded in electron ionisation (EI) mode at 70 eV unless noted otherwise (ESI = electrospray). IR spectra were recorded with 2 cm^{-1} resolution for measurements in KBr, neat, or in solution, and with 1 cm^{-1} resolution for matrix-isolation experiments.

*Methyl 2-[N-methyl-N-(2-pyridyl)aminocarbonyl] acetate **3a***

A mixture of monomethyl malonate **2a** and 2-(methylamino) pyridine **1a** (5 mmol each) in 5 mL of dry (CaH_2) CH_2Cl_2 was treated with DCC (5 mmol) in 5 mL of CH_2Cl_2 with stirring under N_2. After the initial exothermic reaction had subsided, the mixture was allowed to stand for 1 h at room temperature, filtered, the precipitate washed with ether (50 mL), and the combined yellowish filtrates evaporated. The resulting yellow oil was purified by chromatography on a short column (SiO_2, ether) to yield 870 mg (83 %) of **3a** as a colourless oil, turning yellow after exposure to air. ν_{max} (Ar, 14 K)/cm^{-1} 1777 (m), 1771 (m), 1762 (m), 1757 (m), 1754 (m), 1745 (m), 1688 (s), 1624 (m), 1608 (m), 1593 (m), 1484 (m), 1437 (s). δ_H ($CDCl_3$) 8.47 (1H, ddd, *J* 4.9, 2.0, 0.9, H-6), 7.81 (1H, ddd, *J* 7.0, 2.0, 0.9, H-4), 7.31 (1H, ddd, *J* 7.0, 1.0, 0.9, H-3), 7.25 (1H, ddd, *J* 7.0, 4.9, 1.0, 5-H), 3.70 (3H, s, OMe), 3.53 (2H, s, CH_2), 3.42 (3H, s, NMe). δ_C ($CDCl_3$) 167.9 (C=O), 166.0 (C=O), 155.2 (py-C-2)), 148.5, 138.4, 121.8, 119.1, 52.0 (COOMe), 42.4 CH_2), 35.2 (NMe). *m/z* 208 (15 %), 177 (15), 149 (43), 135 (15), 108 (100), 107 (75), 80 (48), 79 (71), 78 (40), 59 (14). HRMS *m/z* 208.0843; calcd for $C_{10}H_{12}N_2O_3$: 208.0848.

*Methyl 2-[N-methyl-N-(2-pyridyl)aminocarbonyl] propanoate **3b***

This compound was prepared in the same manner as described for **3a** and obtained as a colourless oil: 912 mg (85 %). ν_{max} (Ar, 14 K)/cm^{-1} 1766 (sh, m), 1764 (m), 1762 (m), 1757 (m),

1754 (m), 1749 (m), 1697 (s), 1692 (s), 1687 (s), 1683 (m), 1593 (s), 1481 (m) and 1437 (s). δ_H ($CDCl_3$) 8.49 (1H, ddd, *J* 4.9, 2.0, 0.9, H-6), 7.79 (1H, dd, *J* 7.0, 2.0, H-4), 7.28 (1H, ddd, *J* 7.0, 1.0, 0.9, 3-H), 7.24 (1H, ddd, *J* 7.0, 4.9, 1.0, H-5), 3.71 (1H, q, *J* 7.0, CH), 3.67 (3H, s, OMe), 3.53 (2H), 3.41 (3H, s, NMe), 1.39 (3H, d, *J* 7.0, CMe). δ_C ($CDCl_3$) 171.3, 170.1, 155.7, 148.9, 138.5, 122.1, 120.0, 52.3, 44.7, 35.7, 14.3 (C-CH_3). *m/z* 222 ($M^{\cdot+}$, 7 %), 191 (11), 163 (43), 135 (10), 108 (100), 107 (44), 80 (35), 79 (43), 78 (33), 59 (20). *m/z* (ESI) 223 ($[M + H]^{\cdot+}$, 100 %), 222 (35), 163 (40), 109 (30), 108 (45), 107 (30). HRMS *m/z* 222.1004; calcd for $C_{11}H_{14}N_2O_3$: 222.1004. Anal. Calc. for $C_{11}H_{14}N_2O_3$: C 59.45, H 6.35, N 12.60. Found: C 59.33, H 6.39, N 12.55 %.

N-*(2-Pyridyl)chloroacetamide* ***3c***

2-Aminopyridine (0.47 g, 5 mmol) was added to a solution of chloroacetic acid (5 mmol) in 10 mL of CH_2Cl_2. The resulting mixture was treated with DCC (1.03 g, 5 mmol) in 10 mL of CH_2Cl_2 with stirring under N_2. This mixture was kept at 40°C for 2 h and then at room temperature for 15 min, filtered, and the precipitate was washed with dry diethyl ether. The pale brown filtrate was evaporated, and the yellow-brown solid so obtained was purified by chromatography on SiO_2, eluting with diethyl ether/ethyl acetate, to yield 680 mg (80 %) of white crystals which turned red-purple on exposure to air, mp 175°C. GC: a single peak at R_t 7.6 min. *m/z* 172 (6 %), 170 (18), 135 (90), 94 (100), 78 (90). δ_H ($CDCl_3$) 8.35 (d, *J* 4.5, 1H), 8.20 (d, *J* 8.2, 1H), 7.75 (ddd, *J* 8.1, 7.9, 1.3, 1H), 7.71 (ddd, *J* 8.0, 7.8, 1.0, 1H), 4.18 (s, 2H). δ_C ($CDCl_3$) 164.3, 150.1, 147.7, 138.7, 120.5, 113.8, 42.9.

N-(2-Pyridyl)cyanoacetamide **3d** was prepared in the same way as described for **3c** and obtained in 65 % yield (443 mg) of white needles, mp 157°C. GC: one single peak at R_t 7.5 min. *m/z* 161 (29 %), 94 (100), 78 (48). δ_H (DMDO-d_6) 8.31 (d, *J* 8.2, 1H), 8.0 (d, *J* 8.2, 1H), 7.8 (ddd, *J* 7.1, 6.9, 1.5, 1H), 7.13 (ddd, *J* 7.2, 7.0, 1.0, 1H), 3.97 (s, 2H). δ_C (DMSO-d_6) 162.1, 151.3, 148.2, 138.5, 120.0, 115.8, 113.5, 26.8.

N-(2-Pyridyl)diphenylacetamide **3e** was synthesised in the same way as described for **3c** and obtained as a yellow oil, which was purified first by column chromatography as above, then by Kugelrohr distillation at 140°C/10^{-3} hPa in 75 % yield (1.09 g). GC: one single peak at R_t 4.03 min. *m/z* 288 (44 %), 194 (20), 167 (100), 165 (7), 94 (24), 78 (89). δ_H ($CDCl_3$) 8.25 (d, *J* 7.8, 1H), 8.05 (d, *J* 7.0, 1 H), 7.62 (ddd, *J* 7.6, 8.0, 1.5, 1H), 7.26–7.18 (m, 5H), 6.95 (ddd, *J* 7.8, 7.6, 1.5, 1H), 5.0 (s, 1H). δ_C ($CDCl_3$) 171.0, 151.3, 147.3, 138.6, 128.8, 126.9, 119.8, 114.6, 48.0.

N-*(2-Pyridyl)-2-pyridylacetamide* ***3f***

Triethylamine (0.51 g, 5 mmol) was used to neutralise 2-pyridylacetic acid hydrochloride (0.87 g, 5 mmol) in 5 mL of dry CH_2Cl_2. 2-Aminopyridine (0.47 g, 5 mmol) was added, and the resulting mixture was treated with DCC (1.03 g, 5 mmol) in 10 mL of CH_2Cl_2 with stirring under N_2. The reaction was performed and the product worked up as described above to yield 745 mg (70 %) of **3f**, mp 96°C. GC: a single peak at R_t 10.80 min. *m/z* 213 (4 %), 121 (12), 94 (16), 93 (100), 78 (12). δ_H ($CDCl_3$) 8.69 (d, *J* 8.5, 1H), 8.29 (d, *J* 7.2, 1H), 8.20 (d, *J* 8.4, 1H), 7.69 (m, 2H), 7.22 (m, 2H), 7.0 (ddd, *J* 6.9, 7.5, 1.0, 1H), 3.92 (s, 2H). δ_C ($CDCl_3$) 167.8, 154.7, 151.4, 149.5, 147.9, 138.2, 137.3, 124.1, 122.3, 119.6, 114.1, 46.0.

IR Spectra of Ketenes ***4*** *(Ar, 10 K)*

Methoxycarbonylketene **4a**: 2967, 2156, 2152, 2149, 1746, 1719, 1441, 1391, 1354, 1238, 1199, 934, 849, 756 cm^{-1}.

Methoxycarbonyl(methyl)ketene **4b**: 2142, 2136, 2130, 1739, 1729, 1721, 1296, 1290, 1194, 1137, 746, 731 cm^{-1}.

Chloroketene **4c**: 2149, 2143, 1290, 1107, 844, 772 cm^{-1}.

Cyanoketene **4d**: 2239, 2163, 1354, 553 cm^{-1}.

Diphenylketene **4e**: 2106, 1674, 1597, 1293, 694, 485 cm^{-1}.

2-Pyridylketene **4f**: 2132, 2123, 1594, 1586, 1474, 1452, 773 cm^{-1}.

Warm-up of Ketene ***4a*** *and Recombination with Amine* ***1a***

The mixture of ketene **3a** and amine **1a** formed by FVT of **2a** at 420°C was deposited neat on a liquid N_2-cooled KBr target (−196°C) and observed by IR spectroscopy. After warm-up to −130°C, bands due to **3a** and **1a** were observed to decrease with concomitant appearance of the bands due to the precursor **2a**. IR of **3a** and **1a** (neat, −130°C): 2147 (v), 1696 (s), 1521 (m), 1393 (m), 1355 (m), 1247 (s), 1210 (w), 758 (w) cm^{-1}. IR of **2a** (neat, −130°C): 1739 (m), 1642 (s), 1585 (s), 1543 (m), 1469 (m), 1276 (m), 1170 (m) and 1020 (w) cm^{-1}.

Reference Spectra

Reference IR spectra of the following materials in Ar matrices at ~10 K were recorded. A sample of C_3O_2 was prepared by FVT of 2,3-diacetoxysuccinic anhydride at 800°C.[12] C_3O_2: 3065 (m), 2381 (m), 2287 (vs), 2272 (vs). For other IR spectroscopic data for C_3O_2, see ref. [9].

Matrix IR spectra of 2-(methylamino)pyridine **1a** and 2-aminopyridine **1b** have been published previously.[9] 2-(Methylamino)pyridine **1a**: 3504 (m), 3480 (m), 2821 (w), 1617 (s), 1611 (s), 1603 (*v.*), 1524 (s), 1511 (s), 1459 (m), 1421 (s), 1366 (m), 1289 (m), 1156 (m), 981 (w), 771 (s), 734 (m) cm^{-1}. The IR spectra of 2-(methylamino)pyridine **1a**, 2-aminopyridine **1b** (Fig. S3) and 2-picoline (Fig. S4) are shown in the Supplementary Material.

Dimethyl malonate **4**: 1777 (s), 1771 (s), 1765 (s), 1755 (s) and 1747 (s) cm^{-1}.

Methanol was characterised by two absorptions at 3667 and 1034 cm^{-1}.

CO_2 in Ar matrix gives rise to a double band at 2345 and 2341 cm^{-1}.

Supplementary Material

Ar matrix IR spectra of *s-Z-* and *s-E*-2-pyridylketenes **4f** at 10 K and on warm-up, 2-(methylamino)pyridine **1a**, 2-aminopyridine **1b** and 2-picoline **8b**, and ^1H and ^{13}C NMR spectra of amides **3** are available on the Journal's website.

Acknowledgement

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References

[1] (a) T. T. Tidwell, *Ketenes*, 2nd edn **2006** (Wiley: Hoboken, NJ).
(b) *Science of Synthesis (Houben-Weyl)* (Ed. R. L. Danheiser) **2006**, Vol. 23 (Georg Thieme: Stuttgart).
(c) H. Ulrich, *Cumulenes in Click Reactions* **2009** (Wiley: Chichester).
(d) T. T. Tidwell, *Chem. Rev.* **2013**, *113*, 7288.

[2] C. Plüg, C. Wentrup, *Acta Chem. Scand.* **1998**, *52*, 654. doi:10.3891/ACTA.CHEM.SCAND.52-0654

[3] G. Davidovics, M. Monnier, A. Allouche, *Chem. Phys.* **1991**, *150*, 395. doi:10.1016/0301-0104(91)87112-9

[4] For literature IR spectra of cyanoketene from various precursors, see (a) D. W. J. Moloney, M. W. Wong, R. Flammang, C. Wentrup, *J. Org. Chem.* **1997**, *62*, 4240. doi:10.1021/JO9701288
(b) G. Maier, H. P. Reisenauer, K. Rademacher, *Chem. – Eur. J.* **1998**, *4*, 1957. doi:10.1002/(SICI)1521-3765(19981002)4:10<1957::AID-CHEM1957>3.0.CO;2-1
[5] Diphenylketene preparation: (a) E. C. Taylor, A. McKillop, G. H. Hawks, *Org. Synth. Coll. Vol. VI* **1988**, 549.
(b) L. I. Smith, H. H. Hoehn, *Org. Synth. Coll. Vol. III* **1955**, 356.
[6] For IR spectra of diphenylketene and 2-pyridyl isocyanate in Ar matrix, see A. Fiksdahl, C. Wentrup, *ARKIVOC* **2000**, *iii*, 438. doi:10.3998/ARK.5550190.0001.325
[7] H. Staudinger, *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1735. doi:10.1002/CBER.19050380283
[8] 2-Pyridyl isocyanate: A. Fiksdahl, C. Plüg, C. Wentrup, *J. Chem. Soc., Perkin Trans. 2* **2000**, 1841. doi:10.1039/B003662P
[9] 2-Pyridylketene: A. Kuhn, C. Plüg, C. Wentrup, *J. Am. Chem. Soc.* **2000**, *122*, 1945. doi:10.1021/JA993859T
[10] C. Wentrup, *Aust. J. Chem.* **2014**, *67*, 1150.
[11] (a) J. Elguero, C. Marzin, A. R. Katritzky, *The Tautomerism of Heterocycles* **1976** (Academic Press: New York, NY).
(b) I. Alkorta, J. Elguero, *J. Org. Chem.* **2002**, *67*, 1515. doi:10.1021/JO016069M
(c) H. I. Abdulla, M. F. El-Bermani, *Spectrochim. Acta A* **2001**, *57*, 2659. doi:10.1016/S1386-1425(01)00455-3
(d) N. Akai, K. Ohno, M. Aida, *Chem. Phys. Lett.* **2005**, *413*, 306. doi:10.1016/J.CPLETT.2005.07.101
(e) N. Akai, T. Harada, K. Shin-ya, K. Ohno, M. Aida, *J. Phys. Chem. A* **2006**, *110*, 6016. doi:10.1021/JP056290T
[12] L. Crombie, P. A. Gilbert, R. P. Houghton, *J. Chem. Soc. C* **1968**, 130. doi:10.1039/J39680000130