The photochemistry of metyrapone

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Metyrapone [2-methyl-1,2-di(3-pyridyl)propan-2-one, 1] undergoes efficient α-cleavage *via* the $n_O\pi^*$ triplet. The fate of the resulting acyl and alkyl radicals has been determined by transient studies as well as through the isolation of the final products, quantum yield measurements and trapping studies. Processes previously documented for carbocyclic analogues of 1, such as disproportionation and coupling of the alkyl radicals and recombination to the starting compound are here accompanied by another major process, *viz.* coupling with attack of the acyl radical on the pyridine ring, which eventually leads mainly to a polymeric material.

Introduction

Our interest in the photochemistry of heterocyclics and in the photostability of drugs led us to examine the photochemical behaviour of 2-methyl-1,2-di(3-pyridyl)propan-2-one (metyrapone, **1**), a compound used as a diagnostic agent for the determination of pituitary function, the photolability of which is mentioned in the *Pharmacopoeia*,[1] Metyrapone is known to inhibit adrenocortical steroidogenesis since it acts as an antagonist of 11β-hydroxylase and further to inhibit a number of hepatic cytochrome P-450 dependent monooxygenations, such as aromatic ring hydroxylation, and *O*- and *N*-dealkylation.[2,3] The metabolism of this compound has been extensively studied and shown to involve reduction of the carbonyl group to yield metyrapol and *N*-oxidation.[4–6] On the other hand, nothing is known about the actual photodegradation paths. Carbocyclic analogues are known to undergo efficient Norrish Type I cleavage,[7–9] and are used as initiators for polymerization. Mechanistic work has been carried out, and includes kinetic determinations, based both on steady state[7,9] and on flash photolysis experiments.[8]

Results

Spectroscopy

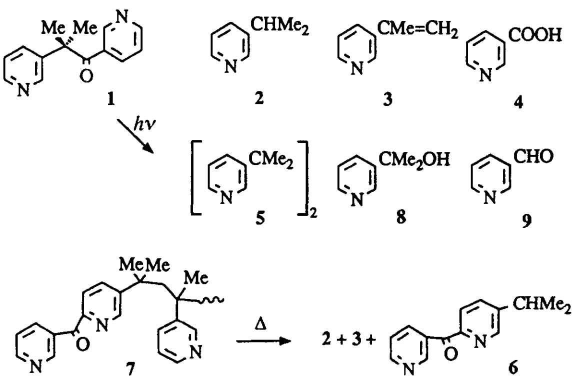
The UV spectrum of **1** in water shows three absorption bands (315 nm, ε 1.9×10^2 dm^3 mol^{-1} cm^{-1}; 264, 5×10^3; 235, 5.9×10^3). In 0.1 M HCl the lowest-energy absorption band is reduced in intensity (ε 60). The spectrum changes little in organic solvents, whether polar or apolar.

While metyrapone does not show any fluorescence, measurements in ether–pentane–alcohol (EPA) glass at 77 K show an intense and structured phosphorescence (λ_{max}/nm 400, 427 and 457), very similar in shape to that observed from 3-acetylpyridine. The emission is affected little in acid-containing glass, while it is red shifted by *ca* 10 nm and is *ca.* 30 times less intense in an apolar glass (2-methylpentane).

A weak emission is also observed in deaerated fluid solution at room temperature in the same wavelength range, and is reduced by about 30% in air-equilibrated solvents.

Photochemistry

Preparative irradiation in deaerated water led to the precipitation of a yellow powder. The filtrate was first examined by vapour phase chromatography (VPC) and showed the presence of 3-isopropylpyridine **2** and of 3-(1-methylethenyl)pyridine **3** (Scheme 1, Table 1). The solution was then evaporated to yield an acetone-insoluble solid, identified as nicotinic acid **4** and an acetone-soluble fraction which was chromatographed to yield a colourless solid identified through its spectroscopic and analytical properties as 2,3-dimethyl-2,3-di(3-pyridyl)butane **5**. The initial precipitate, a material soluble in acetone and methanol, was not amenable to crystallisation nor was it eluted on silica gel by any solvent we checked. Its IR spectrum showed the presence of conjugated carbonyl functions, and the NMR spectrum was typical of a polymer, showing little structure over very broad absorptions. Raising the temperature gave somewhat more detail, with no major change of the overall appearance of the spectrum. The emerging signals could be rationalised as pertaining to several different 3-substituted pyridines. Pyrolysis of this material gave products **2** and **3** in about the same yield as well as a new product isomeric with the starting material. Spectroscopic analysis, in particular the NMR spectrum, showed that this was the 2-pyridyl-3-pyridylketone **6**. Therefore, we suggest that this material is a non-regular polymer, probably with a poly(styrene)-like structure mainly contributing to the chain and pendant 3-pyridylcarbonyl groups as represented in formula **7**.



Scheme 1

The photochemistry was examined in other solvents and gave the same products, although with different yields. In methanol, the polymer **7** did not precipitate during irradiation, but was nevertheless a major product; in most solvents, some alcohol **8** was also formed. In cyclohexane, however, a small amount of pyridine-3-carbaldehyde **9** was detected. Some of the experiments (in water and in methanol) were repeated in air-equilibrated solutions: this caused no change in the product distribution and only a small decrease in the photolysis rate. Addition of a hydrogen donor, dodecane thiol, scarcely affected the product distribution in acetonitrile, but markedly changed

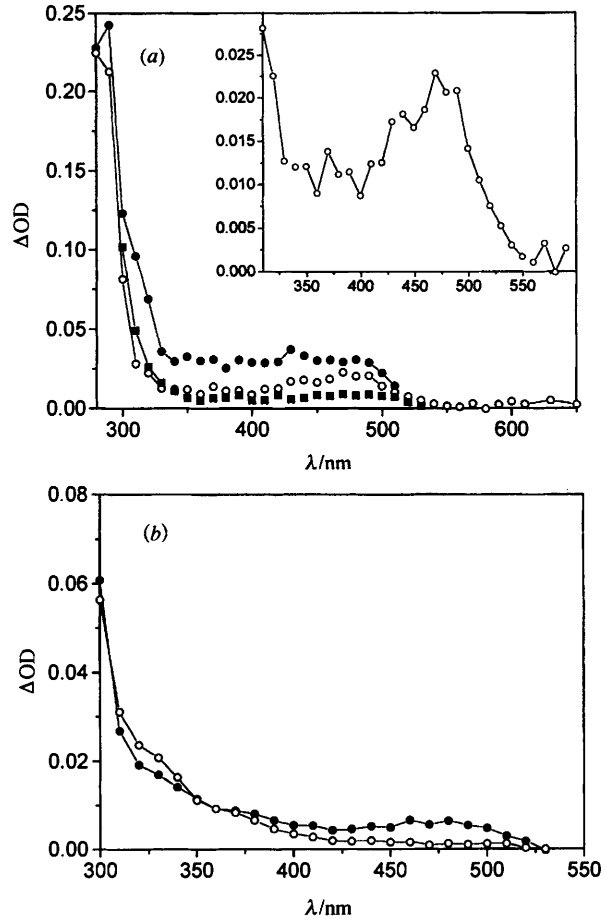


Fig. 1 (*a*) Difference spectra of metyrapone 1.3×10^{-4} M in acetonitrile (argon-saturated solutions) obtained at several delays after 266 nm laser excitation: ●, end-of-pulse spectrum; ○, 50 ns; ■, 2 μs. Inset: scale-expanded spectrum at 50 ns. (*b*) ●, 5 μs; ○, 20 μs.

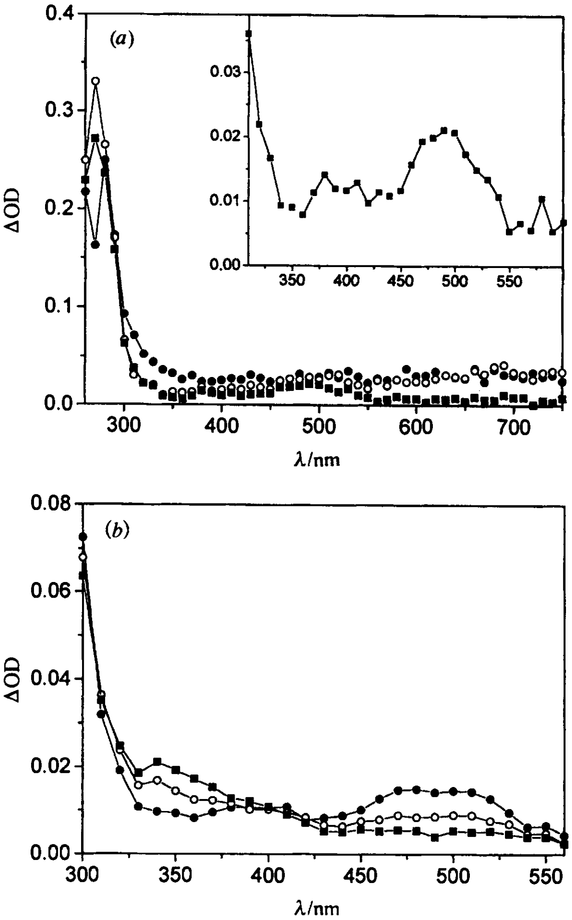


Fig. 2 Difference spectra of metyrapone 1.3×10^{-4} M in water obtained at several delays after 266 nm laser excitation: (*a*) ●, end-of-pulse spectrum; ○, 50 ns; ■, 400 ns (argon saturated solutions). Inset: scale-expanded spectrum at 400 ns. (*b*) ●, 100 ns; ○, 5 μs; ■, 20 μs (N_2O saturated solutions).

the results in cyclohexane, with a drop in the yield of **8** and an increase in the yield of both the bibenzyl **5** and the aldehyde **9**.

The quantum yield of metyrapone decomposition was measured in deaerated cyclohexane and acetonitrile in separate experiments at low conversion. The measured values were 0.44 in the first solvent and 0.79 in the latter.

Flash spectroscopy

Laser excitation (266 nm, 20 ns duration) of a deaerated acetonitrile solution of compound **1** gave an end-of-pulse difference spectrum characterised by a strong absorption band at 290 nm and a broad low-intensity absorption extending in the visible region up to 500 nm [Fig. 1(*a*)]. At > 500 nm, the spectrum was distorted by an emission signal (opposite sign with respect to the other transmission variations). The initial transient showed a first-order decay with lifetime 12 ns (identical to the decay of the above-mentioned emission), leading to the formation of additional transient(s) characterised by an intense absorption at 280 nm as well as a visible band at 480 nm and a shoulder at 430 nm [Fig. 1(*a*), inset]. The decay of this absorption was complex. Analysis by second-order kinetics gave an unsatisfactory fit. In the visible region a fast exponential decay with lifetime of 750 ns was clearly recognised. Two additional slow components with lifetimes of *ca.* 5–6 and 40–50 μs, respectively, were extracted both in the visible and in the UV band, if multiexponential analysis was applied. Concurrently with this decay, an absorption growing between 310 and 350 nm (τ *ca.* 6 μs) was detected [see Fig. 1(*b*)]. Furthermore, long-lived weak absorptions were also detected, *ca.* 415 nm (τ 20 ms) and around 530 nm (τ 7 ms).

Excitation of a deaerated water solution of **1** led to an end-of-pulse difference spectrum characterised by a UV band with maximum at 280 nm and a low-intensity broad band extending beyond the red edge of the visible spectrum [Fig. 2(*a*)]. This spectrum is due to two components, and its time evolution is characterised by two exponential decays, one with τ 12 ns, easily detected between 300 and 400 nm, and one with τ 150 ns, detected in the red part of the spectrum. 400 ns after the pulse the spectrum is characterised by a UV absorption with a maximum at 270 nm and a visible band around 500 nm [see Fig. 2(*a*), inset]. When the experiment was repeated using N_2O-saturated solutions the absorption in the red was no longer observed [Fig. 2(*b*)]. Further evolution of the difference spectrum could be described by multi-exponential kinetics, exhibiting three main components with lifetimes of *ca.* 2, 7 and 45 μs. The 2 μs and 7 μs decay components are linked to the formation of a transient absorbing at *ca.* 340 nm [Fig. 2(*b*)]. Transient species are also detected in the ms range, with absorptions at 385 nm (τ 18 ms) and at 460 nm (τ 5 ms).

Laser excitation of a deoxygenated cyclohexane solution of **1** led to an end-of-pulse spectrum similar to that in acetonitrile (τ 14 ns), and longer-lived transients τ 1.5, 6.5 and 50 μs. The 1.5 μs decay was obtained both from the absorbance in the UV (λ_{max} 290 nm) and in the visible (λ_{max} 470 nm) and was connected to the formation of a further transient absorbing at 310–370 nm. The experiment in cyclohexane was then repeated in the presence of dodecanethiol: this led to quenching of the 1.5 μs transient, at k_q 1×10^9 dm^3 mol^{-1} s^{-1}, while the other two lifetimes were unperturbed, and further to a reduction of the intensity of the 50 μs transient as well as of the absorption at 310–370 nm growing in the μs range.

Discussion

Photophysics

The absorption and low-temperature emission spectra of metyrapone show that the lowest energy chromophore in this molecule is, as expected, the acylpyridine moiety. In the singlet manifold, the $n_N\pi^*$ and the $n_O\pi^*$ transitions are close to one another at *ca.* 78 kcal mol^{-1} (326 kJ mol^{-1}), and in accord with this the ε of the long-wavelength absorption band changes somewhat in protic solvents. The lowest triplet state is unambiguously an $n_O\pi^*$ state, characterised by a structured emission similar to that observed with the carbocyclic analogues.[7] The triplet energy is 73 kcal mol^{-1} (305 kJ mol^{-1}) in protic media and 71.5 kcal mol^{-1} (299 kJ mol^{-1}) in aprotic media. The $n_N\pi^*$ triplet state is also close to the emitting $n_O\pi^*$, and this explains reasonably well the diminished intensity of the phosphorescence in an aprotic glass (since the former state facilitates non-radiative decay) and the greater than expected oxygen quenching of the phosphorescence in solution. The triplet state is also identified by flash-photolysis: the triplet–triplet absorption registered in acetonitrile is quite similar to that of acetophenone in the same solvent, and has the same lifetime as the emission also observed after the flash. Phosphorescence of **1** is indeed observed in a fluid solvent at room temperature also by steady-state irradiation, and is not uncommon with aromatic ketones (*e.g.* it has been observed with deoxybenzoin),[7] although it is seldom strong enough to perturb the transient measurements, as occurs in the present example.

Photochemistry: the primary process

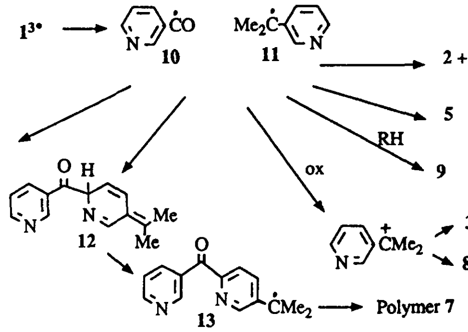
Analogy with related ketones and analysis of the products formed leave no doubt that the rate-determining process in the deactivation of the metyrapone triplet is α-cleavage. The observed lifetime of 12–14 ns, practically independent of solvent, agrees with the occurrence of a strongly thermodynamically favoured fragmentation. For comparison, the measured lifetime for deoxybenzoin, lacking the α,α-disubstitution, is 115 ns in benzene,[8a] and for the dimethyl derivative a lifetime of 8 ns has been evaluated from steady-state measurements.[7,9]

The transient spectrum, observed at the end of the triplet decay, is in agreement with the presence of the pyridyl-acyl and -alkyl radicals **10** and **11**, if it is assumed that the absorption spectra of such species are similar to those of the corresponding phenyl-substituted radicals. This end-of-pulse absorption may contain a further contribution due to products arising from 'in cage' recombination of the primary radical pair (see below). Indeed, radical recombination has been shown to occur at a rate competitive with diffusion 'out of cage' and with configuration change in the α-cleavage of optically active 2-phenylpropiophenone in benzene.[9] Thus, in the cage radical recombination is expected to be faster than triplet decay also in the present case, and part of the chemical process is not revealed by the present detection system.

While most of the transients observed are qualitatively the same in all solvents tested, in water a further band extending to 750 nm is observed. This is attributed to the solvated electron, as confirmed by the absence of such an absorption in N_2O-saturated solutions, since the additive scavenges the electrons within a few nanoseconds.[10] Thus, in water, photoionization competes with α-cleavage of the ketone (see below for the chemical consequence of this process).

Identification of the transients

The processes observed in the microsecond time domain are consistent with non-cage reactions. The radical reactions leading to the final products (see below and Scheme 2) may involve both in- and out-of cage reactions (or a combination of the two). Flash photolysis evidence, however, refers only to the latter reactions. The decay is not second-order, while multiexponential analysis is satisfactory for three first-order decays with similar lifetimes in the solvents tested. In cyclohexane, the shortest-lived transient (1.5 μs) is efficiently quenched by a good hydrogen donor such as dodecanethiol, k_q 1 × 10^9 dm^3 mol^{-1} s^{-1}, and under this condition pyridine-3-carbaldehyde **9** becomes an important product. This supports the identification of this transient as the acyl radical **10**. Reaction of the radical with the solvent can account only in part for the decay (only a small amount of aldehyde **9** is formed in neat cyclohexane, see Table 1). The fact that the decay is pseudo-first order suggests that the main reaction of this transient is coupling either with a radical or with an alkene resulting from the evolution of the primarily formed radical pair (see below). This is the only transient significantly affected by the medium. In water, the lifetime remains at 2 μs, while in acetonitrile it is shorter, 0.75 μs, than in cyclohexane, indeed, in this solvent, radical **10** is not quenched by the thiol. This may correspond to an additional redox path involving the easily reduced acyl radical in a polar, aprotic solvent.



Scheme 2

The 6–7 μs transient, unaffected by the thiol, is tentatively identified as the alkyl radical **11**, which is expected to abstract hydrogen less efficiently than **10**. Benzyl radicals have been revealed by flash photolysis of carbocyclic analogues of **1**.[8b] In the present case, radical **11** is involved in different reactions (see below), and one cannot attribute the observed decay to a specific path. Finally, the 40–50 μs decay is reasonably due to a further radical resulting from a reaction of **10**, since it is less intense, with no change in the lifetime, when its precursor is quenched; a further absorption at *ca.* 330 nm grows in the μs range in a manner parallel to the detriment of shorter-lived transients. These species therefore are secondary radicals, *e.g.* radical **13**, or radicals resulting from the addition of **10** to an alkene (**3** or **12**, see below). Further weak transients are observed in the ms domain. These correspond to the growing radicals in a polymerisation process which finally yields **7**.

Formation of the end-products

While the primary process occurring upon photoexcitation of **1**, α-cleavage from the triplet, is the same as with related carbocyclic ketones, the end-products are in part different, and this is due to different processes from the primarily formed radicals. Thus, dimerization of the benzyl radical **11** to yield product **5** has analogy in other Norrish Type I cleavages, as has the formation of small amounts of the isoproylpyridine **2** and the vinylpyridine **3** by hydrogen exchange. However, these products account for about one third of reacted **1**, while the largest part of the decomposed material is incorporated into the polymer **7**. The structure of the polymer suggests that recombination of the primary radicals **10** and **11** only in part regenerates the starting ketone, while for an important fraction it involves a rather different coupling leading to ketone **12** (Scheme 2). This unsaturated ketone is not expected to be stable under the reaction conditions. As an example, expected paths are hydrogen transfer with rearomatization to yield radical **13**, or addition of the benzoyl radical **10**. In this

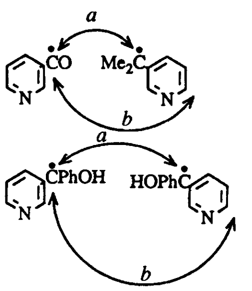
Table 1 Photolysis products from metyrapone **1**

Solvent	Irradiation time/h	Converted **1** (%)	Products (% Yield) **2**	**3**	**4**	**5**	**7**	**8**	**9**
Water	6	95	2	2.5	15	15	50	1	
Methanol	6	95	5	4		35	30	2	
Acetonitrile	6	95	3	2		30	50	2	
'+$C_{12}H_{25}SH$'[a]	6	95	3	2		30	50	2	<0.5
Cyclohexane	6	80	2	4		15	50	15	4
'+$C_{12}H_{25}SH$'[a]	6	80	6	3		25	50	2	20

[a] 2×10^{-3} M.

way, secondary radicals are formed, and these, as well as the primarily formed benzoyl and benzyl radicals **10** and **11** react with the alkenes present (**3** and **12**) leading to the observed polymerisation and thus to the material described above **7**, presumably as a mixture rather than a single structure. The polymerisation process is quite complex, and this accounts for the low-absorbing transients (growing radicals) still observed well into the millisecond range.

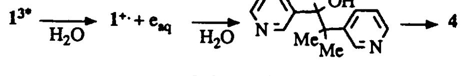
The pyridine nitrogen atom favours radical attack on the ring and this explains why the recombination of the radicals here follows, in part, a path parallel to that leading back to the starting material (see Scheme 3, paths *a* and *b*), a course which is seemingly unimportant with deoxybenzoin and analogues since it has not been reported.[7] One may notice the analogy between the presently observed radical coupling *via* attack to the ring and that occurring with the ketyl radicals formed from 3-benzoylpyridine photoreduction. Also in that case, addition onto the aromatic ring competes with pinacol formation (see Scheme 3, paths *a* and *b*) and no corresponding reaction has been found in the photoreduction of carbocyclic analogue, benzophenone,[11] although the occurrence of a similar ring attack has been postulated in order to explain the observation of anomalous 'light-absorbing transients' in flash photolysis.[11]



Scheme 3

Apparently, this coupling takes place mainly in cage, and once alkene **12** is formed, the ensuing radical-induced polymerisation is little affected by the medium: indeed, the overall process is affected little by solvent or additive changes (see Table 1). The fraction of radicals diffusing out of cage and revealed by flash photolysis leads to the observed low molecular mass products **2**, **3**, **5** and **9**. The alkyl radical **11** in part is oxidised to the cation, in turn revealed by the formation of the alcohol **8**. Apparently escaped radicals **10** are mainly incorporated into the growing polymer, as one would expect from such electrophilic (and probably oxygen-insensitive) radicals, although their presence is revealed with hydrogen-donating solvents (cyclohexane) or additives (RSH).

Photoionization is a completely different process. This occurs only in water, and is revealed both by the identification of the solvated electron as a transient in flash photolysis and by chemical evidence, *viz.* the isolation of a nicotinic acid, a photoproduct not observed in other solvents and in accordance with the solvolysis (by moisture present in the solvent) of the cation radical $\mathbf{1}^{+\bullet}$ (Scheme 4).



Scheme 4

In conclusion, the work on metyrapone shows, similarly to the benzoylpyridine case,[11] that extending the study from carbocyclic to heterocyclic derivatives may contribute to the knowledge of the chemistry of excited states. The end-products distribution is quite complex, and the number of transients superimposed in the same spectral region may appear, at first sight, discouraging. Despite this, the structure of some of the products, coupled with flash photolysis and quenching experiments, gives evidence for paths which are only minor, or not documented, in the Norrish I photochemistry of aryl alkyl ketones, offering a more detailed picture of the chemistry involved, whether in cage or out of cage. In particular in the present case this may be useful in planning the use of ketones subjected to α-cleavage as photoinitiators, since some information has been obtained on how the rate and mode of reaction of the primarily generated radicals depend on the structure.

Experimental

Metyrapone (Aldrich) and the solvents (spectroscopic grade) were used as received. The spectra were measured by means of the following instruments: Cary 19 (UV spectra), Aminco Bowman MPF (fluorescence and phosphorescence, with a phosphoroscope in the latter case), Bruker 300 (NMR), Perkin-Elmer 190 (IR).

Preparative irradiation

A solution of metyrapone (300 mg) in 140 ml water (9.5×10^3 M) was flushed with argon for 10 min and then irradiated by means of a 20 W low-pressure mercury arc in an immersion well apparatus for 30 h. The yellow precipitate was filtered: 150 mg of polymer **7**. The aqueous solution was evaporated and the residue treated with 5 ml acetone. A residue of 15 mg was identified as nicotinic acid **4**. The solution was chromatographed on a silica gel column eluting with ethyl acetate and finally with EtOAc–MeOH 3 : 1 mixture to yield unreacted metyrapone (15 mg), 3-(1-methylethyl)pyridine (**2**, 3 mg), 3-(1-methylethenyl)-pyridine (**3**, 4 mg), 2,3-di(3-pyridyl)-2,3-dimethylbutane (**5**, 23 mg), 3-(1-hydroxy-1-methylethyl)pyridine (**8**, 2 mg), and further nicotinic acid (**4**, 8 mg).

Irradiation in the other solvents was carried out analogously (see Table 1). Nicotinic acid 4 and pyridine-3-carbaldehyde **9** were recognized by comparison with authentic samples. The known alkylpyridines **2**, **3**[12] and **8**[13] gave NMR (*J*/Hz) and MS in accordance with their structures.

2,3-Di(3-pyridyl)-2,3-dimethylbutane **5**, colourless crystals mp 169.5–170.5 °C (acetone) (Calc. for $C_{16}H_{20}N_2O_2$: C, 79.95; H, 8.39; N, 11.66. Found: C, 79.7; H, 8.5; N, 11.6%); $\delta_H(CD_3OD)$

1.4 (Me), 7.3 (dd, *J* 5,8), 7.55 (dt, *J* 2, 8), 8.13 (d, *J* 2), 8.32 (dd, *J* 2, 5); ν_{max}/cm^{-1} 1590, 1570, 1420.

Polymer **7**, light-yellow solid, begins melting at 130 °C, with decomp. is completely molten at 165 °C (Found: C, 72.7; H, 6.1; N, 12.0%); δ_H broad absorptions centred at 1.4, 3.0, 7.2–7.5, 8.2–8.9; ν_{max}/cm^{-1} 1650, 1590.

Pyrolysis of product 7

A 75 mg sample of product **7** was slowly heated in an open tube with a flame. The distillate was dissolved in CH_2Cl_2, the solution was filtered and chromatographed on 10 g silica gel to give compounds **2** (10 mg), **3** (10 mg) and **6** (15 mg).

2-[4-(1-Methylethyl)pyridyl]-3-pyridylmethanone **6**, oil (Calc. for $C_{14}H_{14}N_2O$: C, 74.31, H, 6.24; N, 12.38. Found: C, 74.6; H, 6.4; N, 12.1%); δ_H($CDCl_3$) 1.3 (d, *J* 7, Me), 3.05 (sept, *J* 7, C*H*Me$_2$), 7.45 (dd, *J* 5, 8), 7.8 (dd, *J* 2, 8), 8.1 (d, *J* 8), 8.45 (dt, *J* 2, 8), 8.6 (d, *J* 2), 8.8 (dd, *J* 2, 8), 9.3 (d, *J* 2); δ_C[$(CD_3)_2CO$] 24.0 (Me), 33.0, 124.2 (CH), 125.2 (CH), 133.7; 136.3 (CH), 139.1 (CH), 148.8 (CH), 149.1, 153.0 (CH), 153.4, 153.8 (CH), 192.8; ν_{max}/cm^{-1} 1645; *m/z* 226 (42%), 120 (85), 106 (100).

Quantum yield measurements

These were carried out on 1.5×10^{-1} M solutions of product **1** in spectrophotometric cuvettes after deoxygenation by freeze–degass–thaw cycles by irradiation with a 15 W low-pressure mercury arc. The extent of the reaction was determined by GC and the absorbed flux by oxalate actinometry.

Laser flash photolysis

The set-up for ns time-resolved experiments by excitation at 266 nm has been described previously.[14] The laser (Nd-Yag JK Lasers, 20 ns FWHM, 750 mJ at 1064 nm, frequency quadrupled) was focused on a 3 × 10 mm rectangular area of the cell and the first 2 mm were analysed at right angles. The laser energy used was *ca.* 4 mJ per pulse. Actinometry at 266 nm was performed using a power meter (Scientech) and running the laser at 2 Hz, as in the measurements. The laser energy variations from shot to shot (less than 10%) were detected by using a pyroelectric energy monitor (Laser Precision) to normalize the spectra. Spectral resolution was 2 nm. The sample absorbance was *ca.* 0.6 at 266 nm. The solutions were deoxygenated by bubbling Ar or N_2O during the measurements. Care was taken to renew the solution by changing the sample at each laser shot. The temperature was 294 K. The experimental uncertainty on lifetime values was 15%.

Acknowledgements

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