A study of solvent effect on photochemically induced reactions between pyridinedicarbonitriles and alkenes: an easy approach to the synthesis of cyclopenta[*b* or *c*]pyridines

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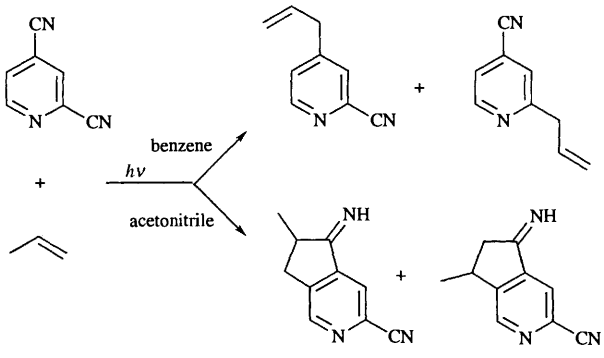
Photochemically induced reactions of pyridinedicarbonitriles and alkenes show an interesting dependence on solvent polarity. In non-polar solvents ipso-substitution of the cyano groups in positions α or γ to the heterocyclic nitrogen occurs to a larger extent, while in polar solvents the reaction provides a path to the formation of a new ring between the carbon atom of one of the cyano groups and a ring position, forming a cyclopenta[*b* or *c*]pyridine derivative (pyridine). Studies on the multiplicity of the excited state controlling the reaction show that the singlet state is involved in the ipso-substitution, while the triplet state controls the formation of the pyridine. An explanation for the solvent effect is given in terms of shift of the excited states with the solvent used. Theoretical calculations justify the position of the cyclisation, although no correlation was found for the regioisomers ratio. This reaction represents an effective entry to the biologically interesting pyridine systems.

A few years ago we reported on a photochemically induced reaction between pyridine-2,4-dicarbonitrile and alkenes in which the solvent was found to play quite a significant role. Indeed, whereas in benzene only ipso-substitution of a cyano group by an allyl group occurs, in acetonitrile a new ring is formed between the alkene, the carbon atom of the cyano group in position 4 and the position 5 of the pyridine ring, so that an imino derivative of the pyrindine is obtained[1] (Scheme 1).

Owing to the biomedical interest in this class of compounds,[2-4] and the fact that other ring closures between the cyano group and the ring have been reported,[5-7] we have extended this study to include other pyridines substituted with two cyano groups. The bases examined were pyridine-2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dicarbonitriles, while the alkenes were cyclopentene (CyPe), 2,3-dimethylbut-2-ene (TME), 1-methylcyclohexene (MeCy), 2-methylpent-2-ene (2Me2), and 2-methylpent-1-ene (2Me1).



Scheme 1

Results and discussion

The products obtained by irradiating pyridine-2,4-dicarbonitrile and alkenes in benzene are shown in Fig. 1 while those obtained in acetonitrile are shown in Fig. 2; yields, isomer ratios and relative reactivities are also reported. Fig. 3 illustrates the products obtained with pyridine-2,6-dicarbonitrile and alkenes together with yields and isomer ratios. For this base as well as pyridine-2,3-, 2,5- and 3,4-dicarbonitriles, both substitution and cyclisation products are formed, the relative amounts depending on the solvent used (Figs. 4–6) (see also the Experimental section). Pyridine-3,5-dicarbonitrile forms only the cyclisation product (Fig. 7).

As we have discussed elsewhere,[8,9] the six-membered heterocyclic bases in their singlet n→π* state can abstract hydrogen atoms, while in their triplet π→π* state, they are able to give rise to electron-transfer reactions. The results of sensitisation and quenching experiments (see Experimental section) indicate that substitution occurs *via* the singlet state while cyclisation occurs *via* the triplet state. It seems reasonable to conclude that the substitution products arise from the abstraction of an allylic hydrogen, with the formation of a pyridinyl radical and an allyl radical which may cross-dimerise and rearomatise to eliminate HCN and form the final product(s), in a manner similar to that reported for the monocyano heterocyclic derivatives.[10] This mechanism may explain why only the cyano group in position α or γ to the heterocyclic nitrogen is substituted. Conversely, the cyclic derivatives are formed by electron transfer from the alkene to the triplet state of the dicyano base with formation of the pyridinyl radical anion and the alkenyl radical cation and subsequent reaction between these two species.[11,12] These findings allowed us to design a kinetic scheme (Scheme 2) from which a kinetic equation [eqn. (1)] may be derived. This equation shows that a linear relationship between the ratio Substitution : Cyclisation (S : C) *vs.* [alkene] should be obtained. This was found true and the parameters for the lines obtained are reported in Table 1. From the first four entries, it is possible to calculate the ratio $K_{et}:K_p$ and these values are: TME = 160, MeCy = 90, CyPe = 10 and 2Me2 = 5.5; because for the same base in the same solvent K_p is the same, K_{et} should be related to the ionisation potential of the alkene; this does not appear from the calculated data, MeCy being more reactive than 2Me2 despite the higher ionisation potential; the reason may lie in the fact that there is a smaller decrease in entropy in building the

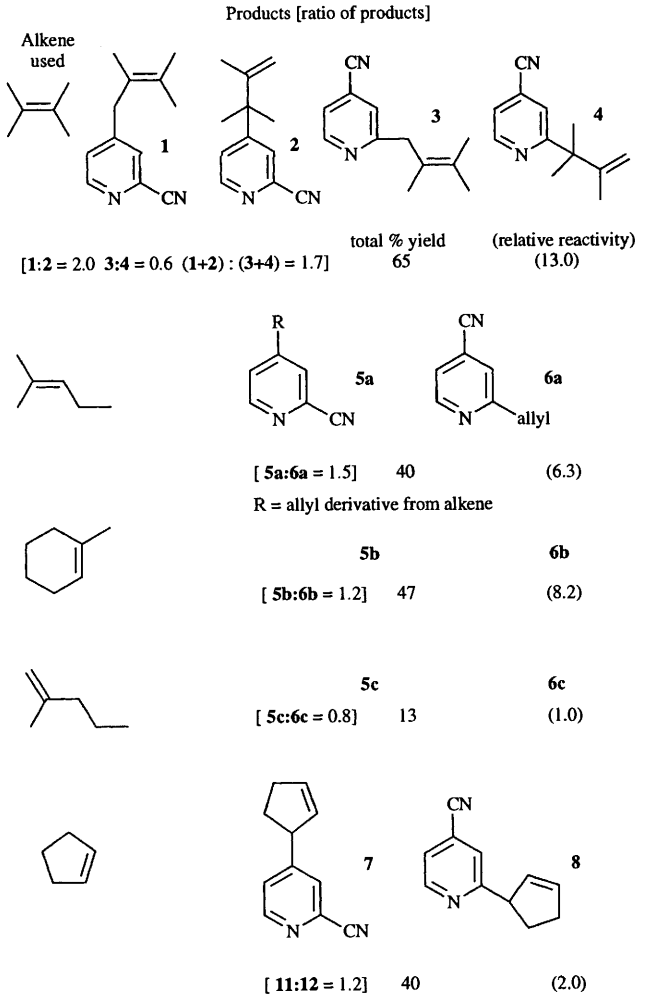


Fig. 1 Allyl derivatives formed in the photochemical reaction between pyridine-2,4-dicarbonitrile and alkenes in benzene solution

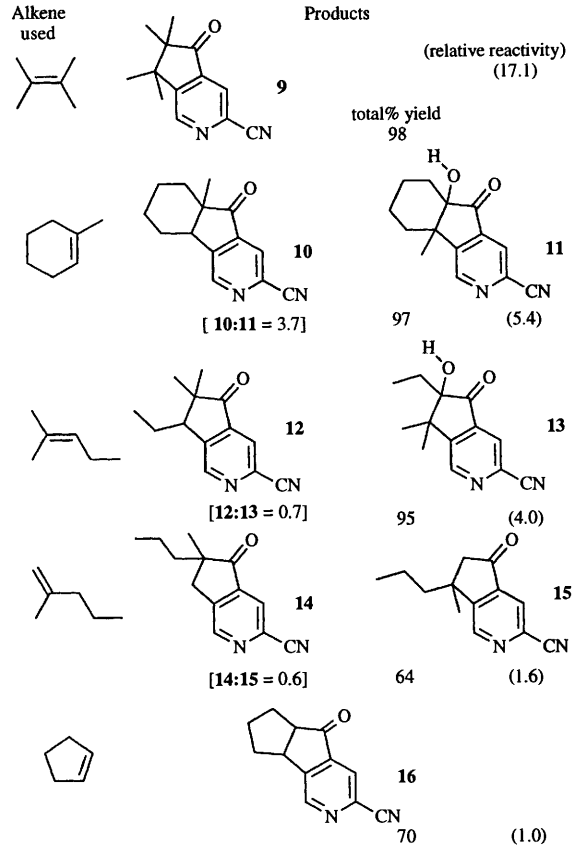


Fig. 2 Pyrindine-derivatives formed in the photochemical reaction between pyridine-2,4-dicarbonitrile and alkenes in acetonitrile solution

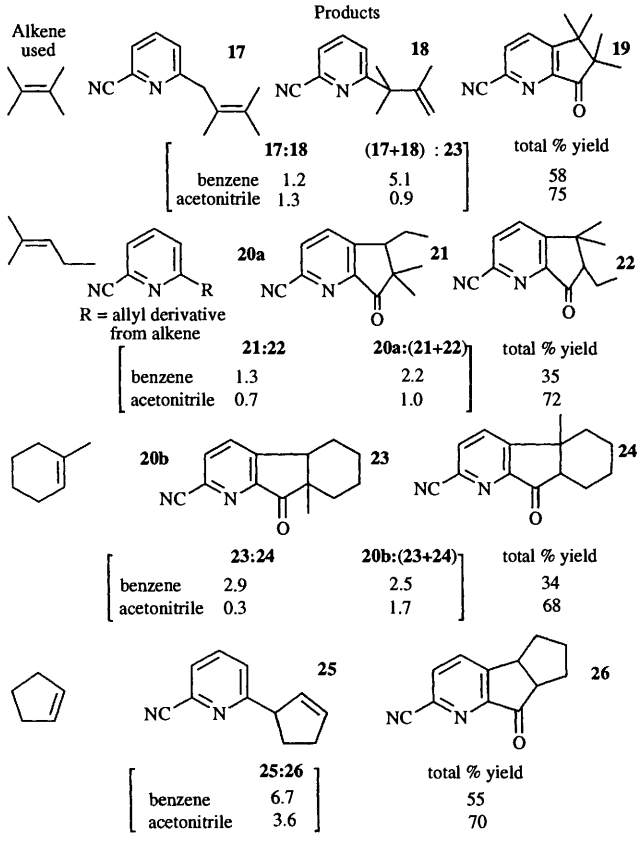


Fig. 3 Pyrindine and allyl derivatives formed in the photochemical reaction between pyridine-2,6-dicarbonitrile and alkenes

new ring starting from a conformation frozen in a cyclic system than from a linear chain; however, in the case of CyPe, the fact that its reactivity is lower than expected, may be related to a higher degree of strain in the connection of two five-membered rings. The same trend in reactivity was also found in the reaction between pyridine-2,4-dicarbonitrile and the different alkenes (Fig. 2).

The dependence on the alkene concentration was found for all the bases that form both the allyl derivative and the pyrindine (Table 1). With the same alkene (TME), k_{et} should be related to the reduction potential of the base. Because we independently determined [13] the K_p values for 2,3- (2.5 10^5 s^{-1}), 2,5- (1.0 10^5 s^{-1}), 2,6- (1.7 10^5 s^{-1}) and 3,4- (1.0 10^5 s^{-1}) dicyanopyridine, we were able to determine the value for k_{et} from the ratio R_1/R_2. The values we found do not agree with the halfwave reduction potential reported in literature.[14]

With respect to the solvent effect, we reported earlier that the fluorescence and the phosphorescence spectra for pyridine-2,4-dicarbonitrile are strongly affected by the kind of solvent used. In non-polar solvents, the fluorescence emission is more intense than the phosphorescence while the reverse is true in polar solvents. This effect, that was found to be general for all the bases under study, was attributed to some mixing of the singlet states S_1 and S_2.[9] The fact that in non-polar solvents the fluorescence emission is more intense than phosphorescence, indicates that intersystem crossing is less favoured. This may explain the general findings that substitution products are obtained to a larger extent in non-polar solvents, while the cyclisation pathway is preferred in polar solvents. The ratio of substitution over cyclisation should be related to the efficiency with which the singlet state is quenched and to the efficiency with which the triplet state is populated.

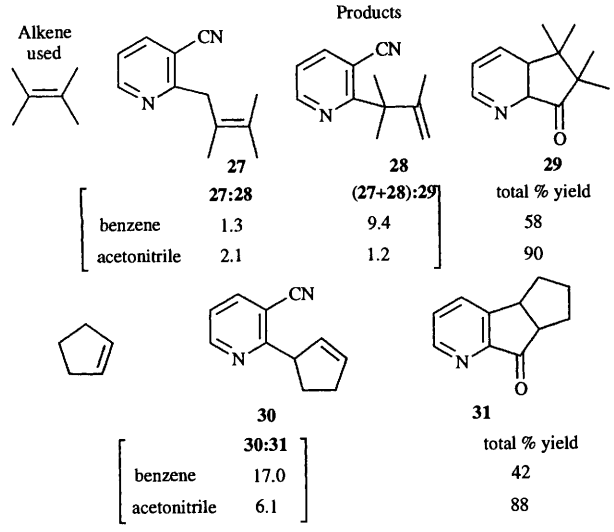


Fig. 4 Pyrindine and allyl derivatives formed in the photochemical reaction between pyridine-2,3-dicarbonitrile and alkenes

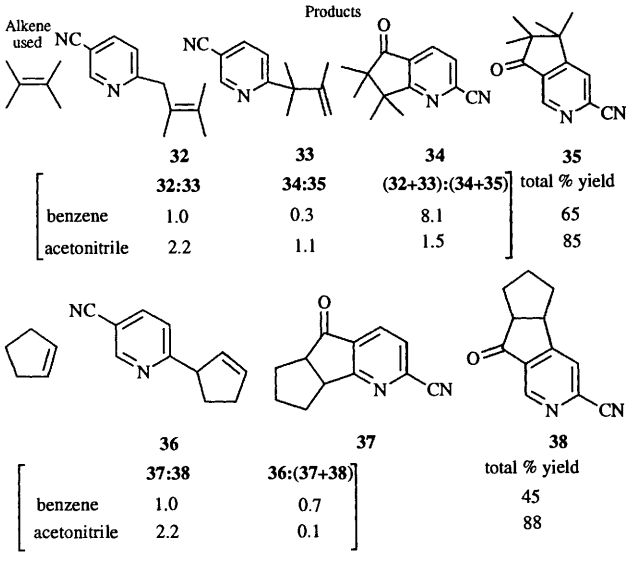


Fig. 5 Pyrindine and allyl derivatives formed in the photochemical reaction between pyridine-2,5-dicarbonitrile and alkenes

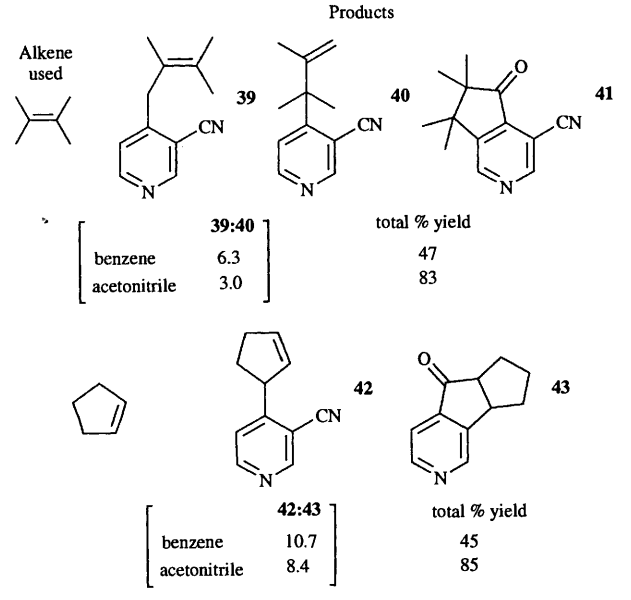


Fig. 6 Pyrindine and allyl derivatives formed in the photochemical reaction between pyridine-3,4-dicarbonitrile and alkenes

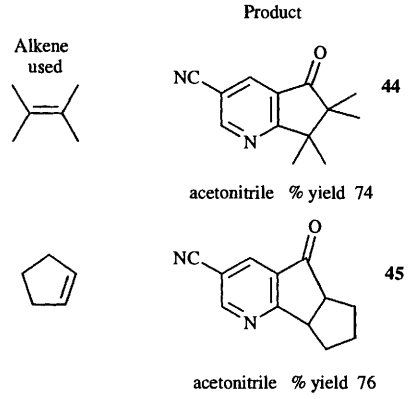


Fig. 7 Pyrindine derivatives formed in the photochemical reaction between pyridine-3,5-dicarbonitrile and alkenes

Indeed, the trend expected from eqn. (1) is followed in different solvents and we may observe a change both in the slope and in the intercept, which is in line with the observation that the lifetimes of singlet and triplet states are influenced by the change in polarity of the solvent (Fig. 8).

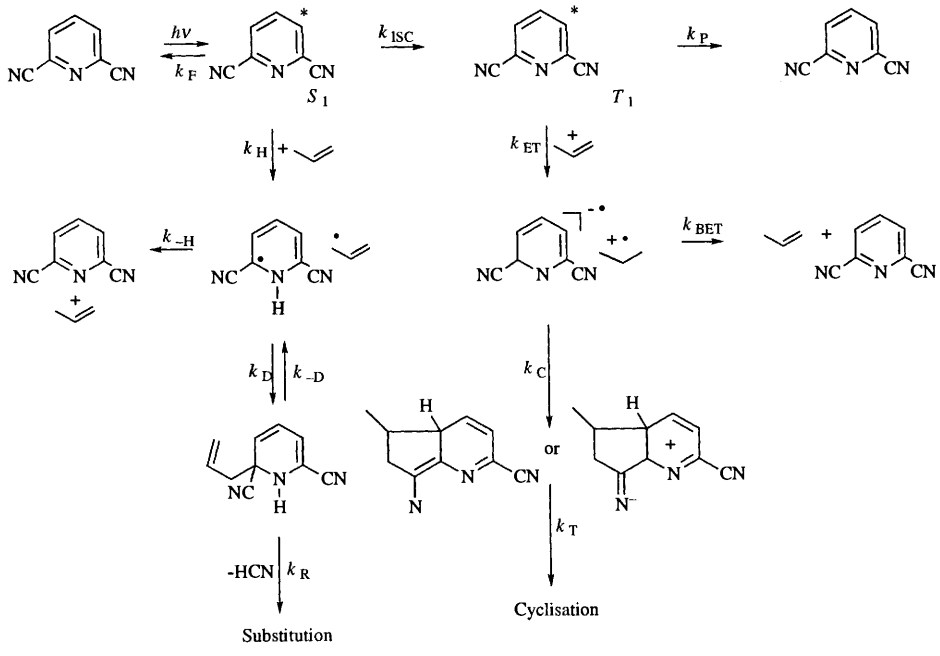
As to the cyclisation, we have found that, with few exceptions, there is a high selectivity with respect to the cyano group as well as the position of the pyridine ring that are involved in the reaction. This selectivity reflects either the spin density or the charge density for the radical anion under consideration. For this reason, theoretical calculations at the level 6-31G+ were performed for the radical anions of the pyridinedicarbonitriles and the values for the charge and the spin densities are reported in Fig. 9 (only for pyridine-3,5-dicarbonitrile was no theoretical self-consistent solution reached, the C_2v symmetry needing to be destroyed for such a result).

Indeed, with the exception of pyridine-2,6-dicarbonitrile, most of the observed selectivities may be explained by assuming the cyano group that is attacked to be the one with the higher negative charge, while the ring position attacked is, in each case, the one with highest spin density. In order to obtain additional information to test our hypothesis about the selectivity of this reaction, analogous calculations at the level 6-31G* were carried out on the radical cations of 2Me2, 2Me1 and MeCy for which different ratios of the regioisomers were found (Fig. 10). Again the trend in the regioisomer distribution may be viewed in terms of cross-coupling of the positions with higher spin density and a combination of the two parts with opposite charge. This expectation was not confirmed. The fact that the ratios in the isomer distributions (Figs. 3–7) show solvent dependence both for the substitution and the cyclisation products, may indicate that the interaction between the two species (the two radicals for the substitution or the two radical ions for the cyclisation) is dependent on their geometry and distance. Such arguments justify the formation of two different products in the reaction between pyridine-3,4-dicarbonitrile and TME or CyPe.

In conclusion, the solvent effect is generally explained in terms of stabilisation of an exciplex in non-polar solvents, while ionic couples are more stabilised in polar solvents.[15] In the photochemistry of this kind of compounds, we believe that the polarity of the solvent plays a role only in the stabilisation of the excited state, and it is the nature of these states that determine the course of the reaction.

Experimental

All the solvents were dried and distilled before use. Pyridine-3,4-dicarbonitrile, cyclopentene, methylcyclohexene, 2-methylpent-2-ene, 2-methylpent-1-ene and 2,3-dimethylbut-2-ene are commercial products and were sublimed or distilled before use. All the other pyridinedicarbonitriles were prepared



Scheme 2

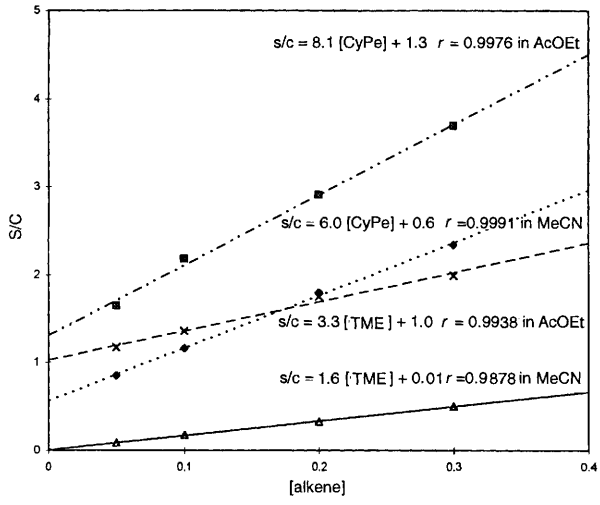


Fig. 8 Plot of the ratio S/C *vs.* [Alkene] for the reaction between pyridine-2,6-dicarbonitrile and TME or CyPe in two different solvents (ethyl acetate and acetonitrile)

$$\frac{dS}{dC} = R_{1^*}[\text{Alkene}] + R_2$$

$$R_1 = \frac{k_R k_H k_D (k_{BET} + k_C)}{k_C k_{ISC}(k_{-D}k_{-H} + k_R k_D + k_R k_{-H})} \qquad (1)$$

$$R_2 = \frac{k_P k_R k_H k_D (k_{BET} + k_C)}{k_{ET} k_C k_{ISC}(k_{-D}k_{-H} + k_R k_D + k_R k_{-H})}$$

$$\frac{R_2}{R_1} = \frac{k_P}{k_{ET}}$$

from the corresponding dicarboxylic acids using the sequence of reactions methyl ester, amide, nitrile as described by Skala.[16] NMR spectra and nuclear Overhauser effects (NOE) were measured in $CDCl_3$ using TMS as internal standard on a 250 MHz spectrometer. 2-H, 3-H, 4-H, 5-H and 6-H refer, respectively, to the hydrogen atom in position 2, 3, 4, 5 and 6 in the pyridine ring for the allyl derivatives, while standard numbering is used for the pyrindines. Mass spectra were recorded on a single focusing spectrometer. Melting points are uncorrected. Standard flash chromatography refers to the procedure reported by W. Clark Still.[17] Solid products obtained from chromatography were sufficiently pure and were not purified further. Gas chromatographic analyses were performed on a 2-m glass column (i.d. 2 mm) packed with 5% SP-1000 at 220 °C or a 2-m glass column (i.d. 2 mm) packed with 10% UCC-W 982 and temperature programmed from 120 to 235 °C (8 °C min^{-1} after the first 4 min) or an OV-1 fused silica capillary column 25 m × 0.25 mm (i.d.) d_f 0.25 mm, carrier gas H_2, linear velocity *ca.* 50 cm s^{-1}; temperature program: 1′ at 40 °C, 20 °C min^{-1} to 150 °C; 2′ at 150 °C, 3 °C min^{-1} to 180 °C, 1′ at 180 °C, 10 °C min^{-1} to 260 °C. A mixture of weighed compounds and standard was used to calibrate the detector response and peak areas were used to determine the product ratios. Fluorescence and phosphorescence spectra were run at liquid nitrogen temperature using acetonitrile or cyclohexane on a JASCO-FP770 equipped with the phosphorimeter. IR spectra were run on Perkin-Elmer Infrared grating spectrometer 177, neat when the product was an oil or in $CHCl_3$ solution when solid. All the photochemical reactions were run in quartz vessels in a RPR-100 Rayonet reactor equipped with 16 low-pressure mercury lamps irradiating at 254 nm. Theoretical calculation at the level 6-31G+ and 6-31G* were performed using the software Gaussian 92;[18] for the pyridinyl

Table 1 Parameters and correlation coefficients for the lines obtained reporting the ratio S/C *vs.* [alkene] for the reactions between pyridine-2,6-dicarbonitrile and TME, MeCy, 2Me2, and CyPe and for the reactions between pyridine-2,3-, -2,5-, -2,6- and -3,4-dicarbonitrile with TME

Alkene	$S/C = R_1^*[\text{Alkene}] + R_2$		r
TME	$R_1 = 1.6$	$R_2 = 0.01$	0.9878
MeCy	$R_1 = 1.8$	$R_2 = 0.03$	0.9957
2Me2	$R_1 = 2.2$	$R_2 = 0.4$	0.9865
CyPe	$R_1 = 6.0$	$R_2 = 0.6$	0.9976
Base	$S/C = R_1^*[\text{TME}] + R_2$		r
3,4-	$R_1 = 66.9$	$R_2 = 0.9$	0.9945
2,3-	$R_1 = 4.6$	$R_2 = 0.4$	0.9758
2,5-	$R_1 = 2.7$	$R_2 = 0.1$	0.9966
2,6-	$R_1 = 1.6$	$R_2 = 0.01$	0.9878

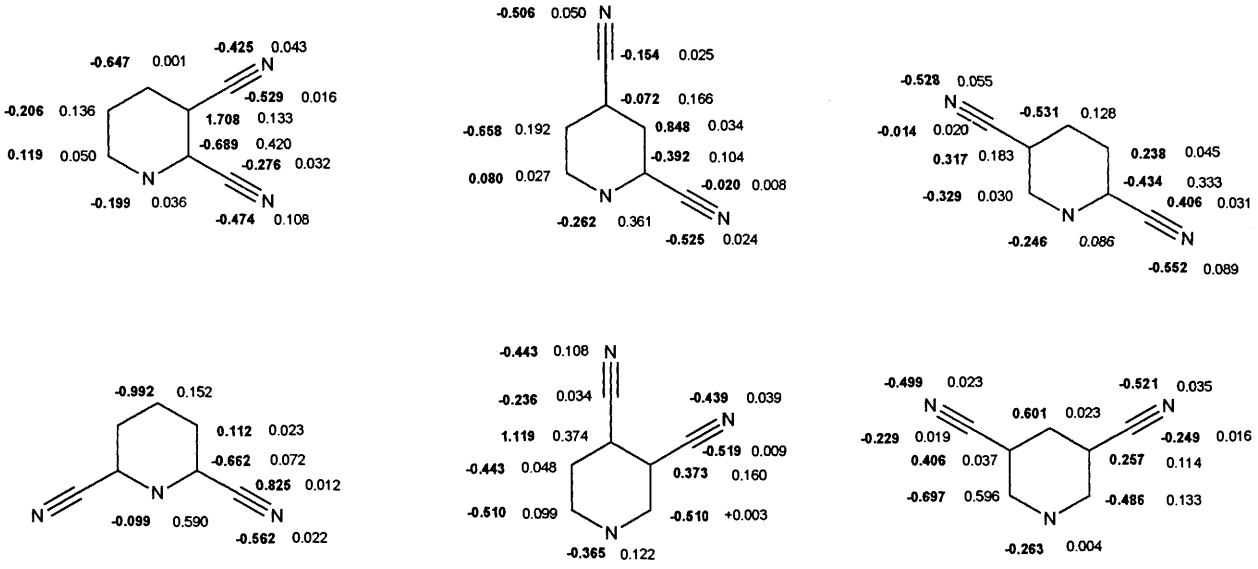


Fig. 9 6-31G + *ab initio* calculations of the electronic distributions and spin densities for the radical anions of the pyridinedicarbonitriles

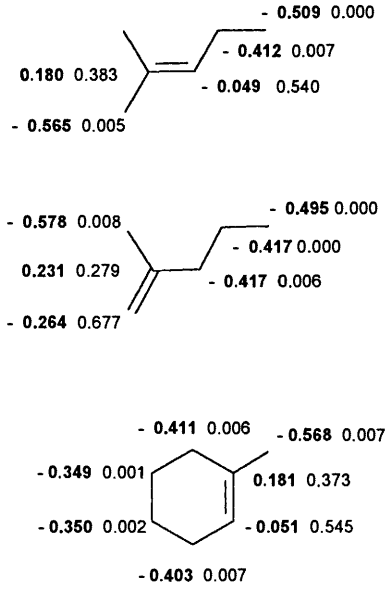


Fig. 10 6-31G* *ab initio* calculations of the electronic distributions and spin densities for the radical cations of 2Me2, 2Me1 and MeCy

radical anions the geometry was optimised assuming a planar structure.

Standard procedure for the preparative reactions

(A) Reactions in benzene. A solution of the appropriate dicyano base (1 mmol) and the alkene (5 mmol) dissolved in benzene (20 cm^3) was irradiated for 19 h after which it was evaporated under reduced pressure. The residue was treated with a 10% aq. hydrochloric acid and the mixture stirred for 2 h. It was then diluted with a large volume of water and extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and evaporated under reduced pressure and the residue was subjected to standard flash chromatography with hexane–ethyl acetate mixtures. The allyl derivatives were completely isolated and identified only in the case of the reactions with TME or CyPe. For the reactions between pyridine-2,4-dicarbonitrile and 2Me2, 2Me1 or MeCy, as well as pyridine-2,6-dicarbonitrile and 2Me2 or MeCy, complex mixtures of all the allyl derivatives were formed. The reaction mixtures were fairly easily separated on a chromatography column. An initial fraction contained all the 2-allylpyridine-4-carbonitrile **6** and the next contained all the 4-allyl isomers **5**; these mixtures were not further fractionated. The position of substitution was determined by MS-GC [the 2-allyl isomers have higher retention times and a stronger $(M-1)^+$ and the pyridine 2-H signal in the NMR spectrum is shifted downfield compared with that for the 4-allyl substituted derivatives].

(B) Reactions in acetonitrile. A solution of the appropriate dicyano base (1 mmol) and the alkene (5 mmol) dissolved in acetonitrile (20 cm^3) was irradiated for 4 h after which it was evaporated under reduced pressure and the residue was treated with a 10% aq. hydrochloric acid and the mixture stirred for 2 h. The resulting solution was basified with ammonia and extracted with CH_2Cl_2. The extract was dried (Na_2SO_4) and evaporated under reduced pressure and the residue was fractionated by standard flash chromatography with CH_2Cl_2–isopropyl alcohol mixtures. With pyridine-2,4-dicarbonitrile and 2MeCy or 2Me2, hydrolysis gives one hydroxylated isomer, **11** or **13** respectively. Confirmation that hydroxylation occurs during work-up was made in the case of 2Me2; after the solvent had been evaporated, isopropyl alcohol was added to the residue and the imino group was reduced to the corresponding amino derivative with $NaBH_4$; subsequent acetylation gave compounds **12a** and **13a**, thereby revealing the identity of the original products. In one case, the mixture from a reaction between pyridine-2,6-dicarbonitrile and TME was separated by chromatography without being previously hydrolysed. This gave together with the allyl derivatives **17** and **18** and the ketone **19**, the original imino pyrindine **19a** (NH replaces O) (20%); the compound was identified on the basis of mass and NMR spectral evidence.

Pyridine-3,4-dicarbonitrile and TME give mainly substitution products, the pyrindine derivative being formed only in very diluted solution (see Fig. 6 and entry 5 in Table 1).

4-(2,3-*Dimethylbut*-2-*enyl*)*pyridine*-2-*carbonitrile* **1**. Oil; δ_H 8.60 (d, 1 H, *J* 5, 6-H), 7.50 (d, 1 H, *J* 1, 3-H), 7.30 (dd, 1 H, *J* 5 and *J* 1, 5-H), 3.48 (s, 2 H, $PyCH_2C$=), 2.80 (s, 6 H, 2 CH_3), 1.60 (s, 3 H, 1 CH_3); *m*/*z* 186, 171 and 156 (Found: C, 76.9; H, 7.7; N, 15.4. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

4-(2,3-*Dimethylbut*-3-*en*-2-*yl*)*pyridine*-2-*carbonitrile* **2**. Oil; δ_H 8.62 (d, 1 H, *J* 5, 6-H), 7.63 (d, 1 H, *J* 1, 3-H), 7.46 (dd, 1 H, *J* 5 and *J* 1, 5-H), 5.05 (m, 2 H, CH_2=), 1.55 (s, 3 H, 1 CH_3), 1.43 (s, 6 H, 2 CH_3); *m*/*z* 186, 172 and 157 (Found: C, 77.9; H, 7.6; N, 14.45. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

2-(2,3-*Dimethylbut*-2-*enyl*)*pyridine*-4-*carbonitrile* **3**. Oil; δ_H 8.70 (d, 1 H, *J* 5, 6-H), 7.30 (m, 2 H, *J* 5, 3-H and 5-H), 3.62 (s, 2 H, $PyCH_2C$=), 1.80 (s, 3 H, 1-CH_3), 1.68 (s, 6 H, 2-CH_3); *m*/*z* 186, 185, 171 and 118 (Found: C, 77.7; H, 7.7; N, 15.5. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

2-(2,3-*Dimethylbut*-3-*en*-2-*yl*)*pyridine*-4-*carbonitrile* **4**. Oil; δ_H 8.73 (d, 1 H, *J* 5, 6-H), 7.50 (d, 1 H, *J* 1, 3-H), 7.30 (dd, 1 H, *J* 5 and *J* 1, 5-H), 5.00 (m, 2 H, CH_2=), 1.60 (s, 3 H, 1 CH_3) and 1.52 (s, 6 H, 2 CH_3); *m*/*z* 186, 185, 171, 156 and 145 (Found: C, 77.8; H, 7.4; N, 15.7. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

4-(*Cyclopent*-2-*enyl*)*pyridine*-2-*carbonitrile* **7**. Oil; δ_H 8.60 (d, 1 H, *J* 5, 6-H), 7.53 (d, 1 H, *J* 1, 3-H), 7.39 (dd, 1 H, *J* 5 and *J* 1, 5-H), 6.10 and 5.85 (both br s, 2 H, CH=CH), 3.95 (br s, 1 H, CHPy) and 2.8–2.2 (br s, 4 H, CH_2CH_2); *m*/*z* 170, 155 and 103 (Found: C, 77.2; H, 6.15; N, 16.9. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%).

2-(*Cyclopent*-2-*enyl*)*pyridine*-4-*carbonitrile* **8**. Oil; δ_H 8.75 (d, 1 H, *J* 5, 6-H), 7.47 (m, 2 H, 3-H, *J* 5, 5-H), 6.10 and 5.80 (both br s, 2 H, CH=CH), 4.00 (br s, 1 H, CHPy), 2.8–2.2 (br s, 4 H, CH_2CH_2); *m*/*z* 170, 169, 155 and 118 (Found: C, 77.1; H, 6.0; N, 16.7. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%).

6,6,7,7-*Tetramethyl*-5-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-3-*carbonitrile* **9**. Mp 98–101 °C; δ_H 9.00 (s, 1 H, 1-H), 7.80 (s, 1 H, 4-H), 1.33 (s, 6 H, 2 CH_3), 1.12 (s, 6 H, 2 CH_3); *m*/*z* 214, 199 and 171; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 72.6; H, 6.7; N, 12.65. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

5a-*Methyl*-5-*oxo*-5a,6,7,8,9,9a-*hexahydro*-5H-*indeno*[1,2-c]-*pyridine*-3-*carbonitrile* **10**. Oil; δ_H 9.02 (s, 1 H, 1-H), 8.01 (s, 1 H, 4-H), 3.24 (t, 1 H, *J* 6, PyC*H*CH_2), 2.2–1.2 [br s, 8 H, $(CH_2)_4$] and 1.30 (s, 3 H, CH_3); *m*/*z* 226, 211, 208, 193, 184 and 155; ν_{max}/cm^{-1} 2230 (conj. CN) and 1740 (CO) (Found: C, 74.1; H, 6.5; N, 12.1. Calc. for $C_{14}H_{14}N_2O$: C, 74.3; H, 6.2; N, 12.4%).

5a-*Hydroxy*-9a-*methyl*-5-*oxo*-5a,6,7,8,9,9a-*hexahydro*-5H-*indeno*[1,2-c]*pyridine*-3-*carbonitrile* **11**. Mp 100–105 °C; δ_H 9.00 (s, 1 H, 1-H), 8.00 (s, 1 H, 4-H), 2.2–0.9 [br s, 8 H, $(CH_2)_4$] and 1.26 (s, 3 H, CH_3); *m*/*z* 242, 225, 210, 196 and 182; ν_{max}/cm^{-1} 3360 (OH), 2240 (conj. CN) and 1730 (CO) (Found: C, 69.9; H, 5.8; N, 11.8. Calc. for $C_{14}H_{14}N_2O_2$: C, 69.4; H, 5.8; N, 11.6%).

7-*Ethyl*-6,6-*dimethyl*-5-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[c]-*pyridine*-3-*carbonitrile* **12**. Oil; δ_H 9.03 (s, 1 H, 1-H), 7.96 (s, 1 H, 4-H), 3.07 (t, 1 H, *J* 7, PyC*H*CH_2), 1.86 and 1.73 (ms, 2 H, C$H_2$$CH_3$), 1.27 (s, 3 H, CH_3C), 1.18 (s, 3 H, CH_3C) and 1.14 (t, 3 H, *J* 7, C$H_3$$CH_2$); NOE values with irradiation of the proton at δ 3.07: H_1 1.4%, CH_2 5.0%, CH_3 0.8 and 0.6%; *m*/*z* 214, 199, 185, 105 and 91; ν_{max}/cm^{-1} 2240 (conj. CN) and 1730 (CO) (Found: C, 73.0; H, 6.8; N, 13.1. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

5-*Acetylamino*-7-*ethyl*-6,6-*dimethyl*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-3-*carbonitrile* **12a** (AcNH *replaces* O). Mp 165–170 °C; δ_H 8.60 (s, 1 H, 1-H), 7.50 (s, 1 H, 4-H), 5.30 (br s, 1 H, NH exch. with D_2O), 4.11 (s, 1 H, CHNH), 2.77 (t, 1 H, *J* 6, C*H*CH_2), 2.17 (s, 3 H, CH_3CO), 1.65 (m, 2 H, C$H_2$$CH_3$), 1.30 (s, 3 H, CH_3C), 1.27 (t, 3 H, *J* 8, C$H_3$$CH_2$) and 0.66 (s, 3 H, CH_3C); *m*/*z* 257, 198, 182 and 169 (Found: C, 69.7; H, 7.6; N, 16.7. Calc. for $C_{15}H_{13}N_2O$: C, 70.0; H, 7.4; N, 16.3%).

6-*Ethyl*-6-*hydroxy*-7,7-*dimethyl*-5-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-3-*carbonitrile* **13**. Mp 123–130 °C; δ_H 9.06 (s, 1 H, 1-H), 7.99 (s, 1 H, 4-H), 3.00 (br s, 1 H, OH exch. with D_2O), 1.90 (q, 2 H, *J* 7, C$H_2$$CH_3$), 1.58 (s, 3 H, CH_3C), 1.26 (s, 3 H, CH_3C), 0.84 (t, 3 H, *J* 7, C$H_3$$CH_2$); *m*/*z* 230, 215 and 173; ν_{max}/cm^{-1} 3360 (OH), 2240 (conj. CN) and 1730 (CO) (Found: C, 67.4; H, 6.3; N, 11.9. Calc. for $C_{12}H_{14}N_2O_2$: C, 76.8; H, 6.1; N, 12.2%).

5-*Acetylamino*-6-*ethyl*-7,7-*dimethyl*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-3-*carbonitrile* **13a**. (AcNH *replaces* O). Oil; δ_H 8.55 (s, 1 H, 1-H), 8.10 (br s, 1 H, NH exch. with D_2O), 7.56 (s, 1 H, 4-H), 4.10 (d, 1 H, CHC*H*NH), 2.32 (m, 1 H, C*H*CH_2), 2.22 (s, 3 H, CH_3CO), 1.40 [s, 6 H, $(CH_3)_2$C], 1.32 (m, 2 H, C$H_2$$CH_3$) and 1.13 (t, 3 H, *J* 7, C$H_3$$CH_2$); *m*/*z* 257, 198, 135 and 93 (Found: C, 71.1; H, 7.2; N, 15.7. Calc. for $C_{15}H_{19}N_3O$: C, 70.0; H, 7.4; N, 16.3%).

6-*Methyl*-5-*oxo*-6-*propyl*-6,7-*dihydro*-5H-*cyclopenta*[c]-*pyridine*-3-*carbonitrile* **14**. Oil; δ_H 9.05 (s, 1 H, 1-H), 8.00 (s, 1 H, 4-H), 3.33 (d, 1 H, *J* 18, HCHPy), 3.01 (d, 1 H, *J* 18, HCHPy), 1.60 (br s, 2 H, CH_2C), 1.25 (br s, 5 H, CH_3C and C$H_2$$CH_3$) and 0.90 (t, 3 H, *J* 5, C$H_3$$CH_2$); *m*/*z* 214, 199, 185 and 172; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 72.1; H, 6.8; N, 13.3. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

7-*Methyl*-5-*oxo*-7-*propyl*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-3-*carbonitrile* **15**. Oil; δ_H 9.01 (s, 1 H, 1-H), 7.92 (s, 1 H, 4-H), 2.83 (d, 1 H, *J* 18, HCHCO), 2.50 (d, 1 H, *J* 18, HCHCO), 1.70 (br s, 2 H, CH_2C), 1.50 (s, 3 H, CH_3C), 1.30 (br s, 2 H, C$H_2$$CH_3$) and 0.90 (t, 3 H, *J* 4, C$H_3$$CH_2$); *m*/*z* 214, 185, 171 and 149; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 72.6; H, 6.8; N, 13.5. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

5-*Oxo*-5,5a,6,7,8,8a-*hexahydropentaleno*[1,2-c]*pyridine*-3-*carbonitrile* **16**. Oil; δ_H 9.15 (s, 1 H, 1-H), 7.92 (s, 1 H, 4-H), 4.03 (m, 1 H, CHPy), 3.21 (m, 1 H, CHCO) and 2.30–1.60 [br s, 6 H, $(CH_2)_3$]; *m*/*z* 198, 180, 169 and 119; ν_{max}/cm^{-1} 2230 (conj. CN) and 1720 (CO) (Found: C, 73.5; H, 5.0; N, 13.6. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

2-(2,3-*Dimethylbut*-2-*enyl*)*pyridine*-6-*carbonitrile* **17**. Oil; δ_H 7.82–7.20 (m, 3 H, 3-H, 4-H and 5-H), 3.61 (s, 2 H, PyCH_2C=), 1.75 (s, 6 H, 2 CH_3) and 1.63 (s, 3 H, 1 CH_3); *m*/*z* 186, 171, 156, 143, 131 and 118 (Found: C, 76.95; H, 7.75; N, 15.35. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

2-(2,3-*Dimethylbut*-3-*en*-2-*yl*)*pyridine*-6-*carbonitrile* **18**. Oil; δ_H 7.80–7.30 (m, 3 H, 3-H, 4-H and 5-H), 4.95 (m, 2 H, CH_2=), 1.53 (s, 3 H, 1 CH_3), 1.48 (s, 6 H, 2 CH_3); *m*/*z* 186, 171, 156, 145, 131 and 118 (Found: C, 77.4; H, 7.7; N, 15.0. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

5,5,6,6-*Tetramethyl*-7-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[b]*pyridine*-2-*carbonitrile* **19**. Mp 165–168 °C; δ_H 8.10 (d, 1 H, *J* 7, 4-H), 7.85 (d, 1 H, *J* 7, 3-H), 1.35 (s, 6 H, 2 CH_3) and 1.29 (s, 6 H, 2 CH_3); *m*/*z* 214, 199, 185, 171 and 156; ν_{max}/cm^{-1} 2230 (conj. CN) and 1740 (CO) (Found: C, 72.8; H, 6.6; N, 13.1. Calc for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

7-*Imino*-5,5,6,6-*tetramethyl*-6,7-*dihydro*-5H-*cyclopenta*[b]-*pyridine*-2-*carbonitrile* **19a** (NH *replaces* O). δ_H 10.40 (br s, 1 H, =NH exch. with D_2O), 7.88 (d, 1 H, *J* 8, 4-H), 7.71 (d, 1 H, *J* 8, 3-H), 1.28 (s, 6 H, 2 CH_3) and 1.22 (s, 6 H, 2 CH_3); *m*/*z* 213, 198, 183, 170 and 156.

5-*Ethyl*-6,6-*dimethyl*-7-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[b]-*pyridine*-2-*carbonitrile* **21**. Mp 107–110 °C; δ_H 8.18 (d, 1 H, *J* 7, 4-H), 7.80 (d, 1 H, *J* 7, 3-H), 3.00 (t, 1 H, *J* 7, PyC*H*CH_2), 1.80 (m, 2 H, *J* 7 and *J* 6, CHC$H_2$$CH_3$), 1.31 (s, 3 H, CH_3C), 1.20 (s, 3 H, CH_3C) and 1.19 (t, 3 H, *J* 6, C$H_3$$CH_2$); *m*/*z* 214, 199, 185, 105 and 91; ν_{max}/cm^{-1} 2250 (conj. CN) and 1740 (CO) (Found: C, 73.1; H, 6.4; N, 13.3. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

6-*Ethyl*-5,5-*dimethyl*-7-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[b]-*pyridine*-2-*carbonitrile* **22**. Oil; δ_H 7.98 (d, 1 H, *J* 7, 4-H), 7.80 (d, 1 H, *J* 7, 3-H), 4.10 (q, 1 H, *J* 8, CH_2C*H*CO), 1.85 (m, 2 H, *J* 8 and *J* 5, CHC$H_2$$CH_3$), 1.52 (s, 3 H, CH_3C), 1.36 (s, 3 H, CH_3C), 1.18 (t, 3 H, *J* 5, C$H_3$$CH_2$); *m*/*z* 214, 213, 199 and 185; ν_{max}/cm^{-1} 2250 (conj. CN) and 1740 (CO) (Found: C, 72.0; H, 6.7; N, 13.4. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

8a-*Methyl*-9-*oxo*-5,6,7,8,8a,9-*hexahydro*-4bH-*indeno*[2,1-b]-*pyridine*-2-*carbonitrile* **23**. Oil; δ_H 8.02 (d, 1 H, *J* 7, 4-H), 7.83 (d, 1 H, *J* 7, 3-H), 3.14 (t, 1 H, *J* 6, PyC*H*CH_2), 2.4–1.1 [br s, 8 H, $(CH_2)_4$] and 1.34 (s, 3 H, CH_3); *m*/*z* 226, 211, 197, 170 and 155; ν_{max}/cm^{-1} 2240 (conj. CN) and 1720 (CO) (Found: C, 73.9; H, 6.4; N, 12.7. Calc. for $C_{14}H_{14}N_2O$: C, 74.3; H, 6.2; N, 12.4%).

4b-*Methyl*-9-*oxo*-5,6,7,8,8a,9-*hexahydro*-4bH-*indeno*[2,1-b]-*pyridine*-2-*carbonitrile* **24**. Oil; δ_H 8.01 (d, 1 H, *J* 7, 4-H), 7.81 (d, 1 H, *J* 7, 3-H), 4.12 (dd, 1 H, *J* 6, CH_2C*H*CO), 2.1–1.1 [br s, 8 H, $(CH_2)_4$] and 1.22 (s, 3 H, CH_3); *m*/*z* 226, 211, 197 and 170; ν_{max}/cm^{-1} 2240 (conj. CN) and 1720 (CO) (Found:

C, 75.4; H, 6.0; N, 12.05. Calc. for $C_{14}H_{14}N_2O$: C, 74.3; H, 6.2; N, 12.4%).

6-(*Cyclopent*-2-*enyl*)*pyridine*-2-*carbonitrile* **25**. Oil; δ_H 7.80–7.30 (m, 3 H, 3-H, 4-H and 5-H), 5.93 and 5.72 (both br s, 2 H, CH=CH), 4.10 (br s, 1 H, PyCH) and 2.60 (m, 4 H, CH_2CH_2); *m*/*z* 170, 169, 155 and 142 (Found: C, 78.1; H, 5.8; N, 16.0. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%).

8-*Oxo*-4b,5,6,7,7a,8-*hexahydropentaleno*[2,1-b]*pyridine*-2-*carbonitrile* **26**. Mp 145–150 °C; δ_H 8.08 (d, 1 H, *J* 7, 4-H), 7.80 (d, 1 H, *J* 7, 3-H), 3.83 and 3.19 (m, 2 H, PyCHCHCO) and 2.0 [br s, 6 H, $(CH_2)_3$]; *m*/*z* 198, 179, 169, 155 and 142; ν_{max}/cm^{-1} 2240 (conj. CN) and 1735 (CO) (Found: C, 72.5; H, 5.25; N, 14.1. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

2-(2,3-*Dimethylbut*-2-*enyl*)*pyridine*-3-*carbonitrile* **27**. Oil; δ_H 8.76 (dd, 1 H, *J* 5 and *J* 2, 6-H), 7.80 (dd, 1 H, *J* 2 and *J* 7, 4-H), 7.25 (dd, 1 H, *J* 5 and *J* 7, 5-H), 3.84 (s, 2 H, $PyCH_2C$=) and 1.86, 1.72, 1.60 (all s, 9 H, 3 CH_3); *m*/*z* 186, 185, 171, 156 and 148 (Found: C, 77.55; H, 7.75; N, 14.65. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

2-(2,3-*Dimethylbut*-3-*en*-2-*yl*)*pyridine*-3-*carbonitrile* **28**. Oil; δ_H 8.77 (dd, 1 H, *J* 5 and *J* 2, 6-H), 7.93 (dd, 1 H, *J* 2 and *J* 7, 4-H), 7.25 (dd, 1 H, *J* 5 and *J* 7, 5-H), 4.89 (m, 2 H, CH_2=), 1.70 (s, 3 H, 1 CH_3) and 1.60 (s, 6 H, 2 CH_3); *m*/*z* 186, 185, 171, 156 and 145 (Found: C, 77.6; H, 7.5; N, 15.0. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

5,5,6,6-*Tetramethyl*-7-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[b]*pyridine* **29**. Oil; δ_H 8.77 (dd, 1 H, *J* 5 and *J* 2, 2-H), 7.98 (dd, 1 H, *J* 2 and *J* 7, 4-H), 7.28 (dd, 1 H, *J* 5 and *J* 7, 3-H), 1.30 (s, 6 H, 2 CH_3) and 1.14 (s, 6 H, 2 CH_3); *m*/*z* 189, 174, 146 and 130; ν_{max}/cm^{-1} 1715 (CO) (Found: C, 75.6; H, 8.3; N, 7.3. Calc. for $C_{12}H_{15}NO$: C, 76.2; H, 8.0; N, 7.4%).

2-(*Cyclopent*-2-*enyl*)*pyridine*-3-*carbonitrile* **30**. Oil; δ_H 8.71 (dd, 1 H, *J* 5 and *J* 2, 6-H), 7.69 (dd, 1 H, *J* 2 and *J* 8, 4-H), 7.20 (dd, 1 H, *J* 5 and *J* 8, 5-H), 5.72 (br s, 2 H, CH=CH), 4.11 (m, 1 H, PyCH) and 2.80 (m, 4 H, CH_2CH_2); *m*/*z* 170, 169, 155 and 142 (Found: C, 77.35; H, 6.1; N, 16.3. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%).

4b,5,6,7,7a,8-*Hexahydropentaleno*[2,1-b]*pyridin*-8-*one* **31**. Oil; δ_H 8.80 (dd, 1 H, *J* 4 and *J* 1, 2-H), 7.91 (dd, 1 H, *J* 1 and *J* 7, 4-H), 7.28 (dd, 1 H, *J* 4 and *J* 7, 3-H), 3.80 (m, 1 H, Py*CH*CH_2), 3.18 (m, 1 H, CH_2*CH*CO) and 2.10 [br s, 6 H, $(CH_2)_3$]; *m*/*z* 173, 145, 144 and 117; ν_{max}/cm^{-1} 1710 (CO) (Found: C, 76.95; H, 6.4; N, 8.0. Calc. for $C_{11}H_{11}NO$: C, 76.3; H, 6.5; N, 8.1%).

2-(2,3-*Dimethylbut*-2-*enyl*)*pyridine*-5-*carbonitrile* **32**. Oil; δ_H 8.80 (dd, 1 H, *J* 1, 6-H), 7.85 (dd, 1 H, *J* 1 and *J* 7, 4-H), 7.22 (dd, 1 H, *J* 7, 3-H), 3.66 (s, 2 H, $PyCH_2C$=) and 1.74, 1.72, 1.66 (all s, 9 H, 3 CH_3); *m*/*z* 186, 185, 171 and 156 (Found: C, 77.8; H, 7.6; N, 14.5. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

2-(2,3-*Dimethylbut*-3-*en*-2-*yl*)*pyridine*-5-*carbonitrile* **33**. Oil; δ_H 8.84 (dd, 1 H, *J* 1, 6-H), 7.86 (dd, 1 H, *J* 1 and *J* 7, 4-H), 7.42 (dd, 1 H, *J* 7, 3-H), 5.00 (m, 2 H, CH_2=), 1.55 (s, 3 H, 1 CH_3) and 1.49 (s, 6 H, 2 CH_3); *m*/*z* 186, 185, 171 and 156 (Found: C, 76.6; H, 7.8; N, 15.4. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

6,6,7,7-*Tetramethyl*-5-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[b]*pyridine*-2-*carbonitrile* **34**. Mp 88–91 °C; δ_H 8.10 (d, 1 H, *J* 6, 4-H), 7.71 (d, 1 H, *J* 6, 3-H), 1.30 (s, 6 H, 2 CH_3) and 1.16 (s, 6 H, 2 CH_3); *m*/*z* 214, 199, 171, 155 and 142; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 72.95; H, 6.4; N, 13.4. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

5,5,6,6-*Tetramethyl*-7-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-3-*carbonitrile* **35**. Mp 104–106 °C; δ_H 8.99 (s, 1 H, 1-H), 7.87 (s, 1 H, 4-H), 1.28 (s, 6 H, 2 CH_3) and 1.13 (s, 6 H, 2 CH_3); *m*/*z* 214, 199, 171 and 155; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 73.9; H, 6.4; N, 12.7. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

2-(*Cyclopent*-2-*enyl*)*pyridine*-5-*carbonitrile* **36**. Oil; δ_H 8.80 (dd, 1 H, *J* 1, 6-H), 7.82 (dd, 1 H, *J* 1 and *J* 8, 4-H), 7.26 (dd, 1 H, *J* 8, 3-H), 6.00 and 5.72 (m, 2 H, CH=CH), 4.15 (m, 1 H, PyCH) and 2.70–2.00 (m, 4 H, CH_2CH_2); *m*/*z* 170, 169, 155, 142 and 129 (Found: C, 77.1, H, 6.15; N, 16.7. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%).

5-*Oxo*-5,5a,6,7,8,8a-*hexahydropentaleno*[1,2-b]*pyridine*-2-*carbonitrile* **37**. Oil; δ_H 8.05 (d, 1 H, *J* 6, 4-H), 7.78 (d, 1 H, *J* 6, 3-H), 3.15 and 2.68 (m, 2 H, PyCHCHCO), 1.60 [m, 6 H, $(CH_2)_3$]; *m*/*z* 198 and 170; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 72.0; H, 5.3; N, 14.9. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

8-*Oxo*-4b,5,6,7,7a,8-*hexahydropentaleno*[2,1-c]*pyridine*-3-*carbonitrile* **38**. Oil; δ_H 8.95 (s, 1 H, 1-H), 6.90 (s, 1 H, 4-H), 3.15 and 2.68 (m, 2 H, PyCHCHCO) and 1.60 [m, 6 H, $(CH_2)_3$]; *m*/*z* 198 and 170; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 72.3; H, 5.2; N, 13.95. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

4-(2,3-*Dimethylbut*-2-*enyl*)*pyridine*-3-*carbonitrile* **39**. Oil; δ_H 8.80 (s, 1 H, 2-H), 8.66 (d, 1 H, *J* 5, 6-H), 7.29 (d, 1 H, *J* 5, 5-H), 3.66 (s, 2 H, $PyCH_2C$=), 1.81 (s, 6 H, 2 CH_3) and 1.63 (s, 3 H, 1 CH_3); *m*/*z* 186, 171, 156, 145 and 131 (Found: C, 76.9; H, 7.9; N, 15.2. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

4-(2,3-*Dimethylbut*-3-*en*-2-*yl*)*pyridine*-3-*carbonitrile* **40**. Oil; δ_H 8.80 (s, 1 H, 2-H), 8.72 (d, 1 H, *J* 5, 6-H), 7.46 (d, 1 H, *J* 5, 5-H), 5.05 and 4.86 (both s, 2 H, CH_2=), 1.67 (s, 3 H, 1 CH_3) and 1.58 (s, 6 H, 2 CH_3); *m*/*z* 186, 185, 171, 145 and 131 (Found: C, 77.9; H, 7.7; N, 14.45. Calc. for $C_{12}H_{14}N_2$: C, 77.4; H, 7.6; N, 15.0%).

6,6,7,7-*Tetramethyl*-5-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[c]*pyridine*-4-*carbonitrile* **41**. Oil; δ_H 9.10 (s, 1 H, 3-H), 8.92 (s, 1 H, 1-H), 1.36 (s, 6 H, 2 CH_3) and 1.15 (s, 6 H, 2 CH_3); *m*/*z* 214, 199, 185 and 171; ν_{max}/cm^{-1} 2230 (conj. CN) and 1730 (CO) (Found: C, 73.5; H, 7.7; N, 12.8. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

4-(*Cyclopent*-2-*enyl*)*pyridine*-3-*carbonitrile* **42**. Oil; δ_H 8.70 (s, 1 H, 2-H), 8.58 (d, 1 H, *J* 5, 6-H), 8.16 (d, 1 H, *J* 5, 5-H), 6.08 and 5.68 (m, 2 H, CH=CH), 4.23 (m, 1 H, PyCH) and 2.52 (m, 4 H, CH_2CH_2); *m*/*z* 170, 169, 155 and 142 (Found: C, 78.2; H, 5.8; N, 16.0. Calc. for $C_{11}H_{10}N_2$: C, 77.6; H, 5.9; N, 16.5%).

8,8a,6,7,5,5a-*Hexahydropentaleno*[1,2-b]*pyridin*-5-*one* **43**. Oil; δ_H 8.81 (s, 1 H, 1-H), 8.58 (d, 1 H, *J* 5, 3-H), 7.50 (d, 1 H, *J* 5, 4-H), 3.89 and 3.11 (m, 2 H, PyCHCHCO) and 2.20–1.50 [m, 6 H, $(CH_2)_3$]; *m*/*z* 173, 145, 132 and 117; ν_{max}/cm^{-1} 1730 (CO) (Found: C, 76.6; H, 6.2; N, 8.25. Calc. for $C_{11}H_{11}NO$: C, 76.3; H, 6.4; N, 8.1%).

6,6,7,7-*Tetramethyl*-5-*oxo*-6,7-*dihydro*-5H-*cyclopenta*[b]*pyridine*-3-*carbonitrile* **44**. Mp 65–70 °C; δ_H 9.00 (d, 1 H, *J* 2, 2-H), 8.20 (s, 1 H, *J* 2, 4-H), 1.30 (s, 6 H, 2 CH_3) and 1.13 (s, 6 H, 2 CH_3); *m*/*z* 214, 199, 171 and 155; ν_{max}/cm^{-1} 2240 (conj. CN) and 1730 (CO) (Found: C, 72.3; H, 6.5; N, 13.4. Calc. for $C_{13}H_{14}N_2O$: C, 72.9; H, 6.6; N, 13.1%).

5-*Oxo*-8,8a,6,7,5,5a-*hexahydropentaleno*[1,2-b]*pyridine*-3-*carbonitrile* **45**. Mp 102–106 °C; δ_H 9.01 (d, 1 H, *J* 2, 2-H), 8.20 (s, 1 H, *J* 2, 4-H), 3.85 (m, 1 H, CHPy), 3.19 (m, 1 H, CHCO) and 2.08 [m, 6 H, $(CH_2)_3$]; *m*/*z* 198, 170, 169, 155 and 142; ν_{max}/cm^{-1} 2240 (conj. CN) and 1725 (CO) (Found: C, 73.0; H, 5.0; N, 14.5. Calc. for $C_{12}H_{10}N_2O$: C, 72.7; H, 5.1; N, 14.1%).

Sensitisation and quenching experiments

Pyridine-2,6-dicarbonitrile (singlet energy 418 kJ mol^{-1}, triplet energy 299 kJ mol^{-1}) (1 mmol) and 2,3-dimethylbut-2-ene (5 mmol) were dissolved in acetonitrile (20 cm^3) saturated with a large excess of piperylene (triplet energy 248 kJ mol^{-1}).[19] The solution was irradiated at 254 nm for 5 h after which it was evaporated under reduced pressure. The residue, examined by GC, whilst containing substitution products contained no trace of the imino or the ketone derivative.

Acetophenone (singlet energy 329 kJ mol^{-1}, triplet energy 308–310 kJ mol^{-1})[19] (1 mmol) was added to a solution of pyridine-2,6-dicarbonitrile (1 mmol) and 2,3-dimethylbut-2-ene (5 mmol) in benzene (20 cm^3). After the solution had been irradiated for 19 h at 350 nm (a wavelength at which the light is absorbed only by the ketone) it was evaporated under reduced pressure and the residue examined by GC. Only a peak

corresponding to the imino derivative was present. After hydrolytic treatment of the residue, the ketone was detected and isolated.

Competitive reactions

Standard procedures (A or B) were followed except that instead of a single selected alkene, equimolar amounts of two different alkenes were added. At the end of the irradiation time, a standard was added and the mixtures were both analysed directly or hydrolysed and analysed by GC.

Alkene concentration effect

Two stock solutions were prepared: one of the appropriate dicyano base in acetonitrile (concentration 10^{-2} mol dm^{-3}) and the other of the alkene under study (0.8 mol dm^{-3}). The first solution was charged into four quartz vessels followed by sufficient of the second solution to give relative ratios of alkene to base of 2, 4, 8, 12:1. The total volume of each mixture was adjusted to 20 cm^3 by the addition of acetonitrile. For pyridine-2,6-dicarbonitrile the same procedure was followed except that ethyl acetate was used as solvent. The solutions were irradiated at 254 nm for 2 h after which a weighed quantity of benzophenone was added as internal standard. The determination of the relative amounts of the substitution *vs.* cyclisation was made on the original solution as well as that resulting from the hydrolysis. The results were accurate to within the limits of experimental error. This procedure was followed for all the bases reported with the exception of the pyridine-3,4-dicarbonitrile for which the ratios of alkene to base were 2, 3, 4, 5:1.

Solvent effect

A solution of pyridine-2,6-dicarbonitrile (1 mmol) and TME (5 mmol) in either ethyl acetate or acetonitrile (20 cm^3) was irradiated for 2 h after which a weighed quantity of benzophenone was added as internal standard. A determination of the relative amounts of substitution *vs.* cyclisation was made on the original solution as well as the one resulting from the hydrolysis. The results were accurate to within limits of experimental error.

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