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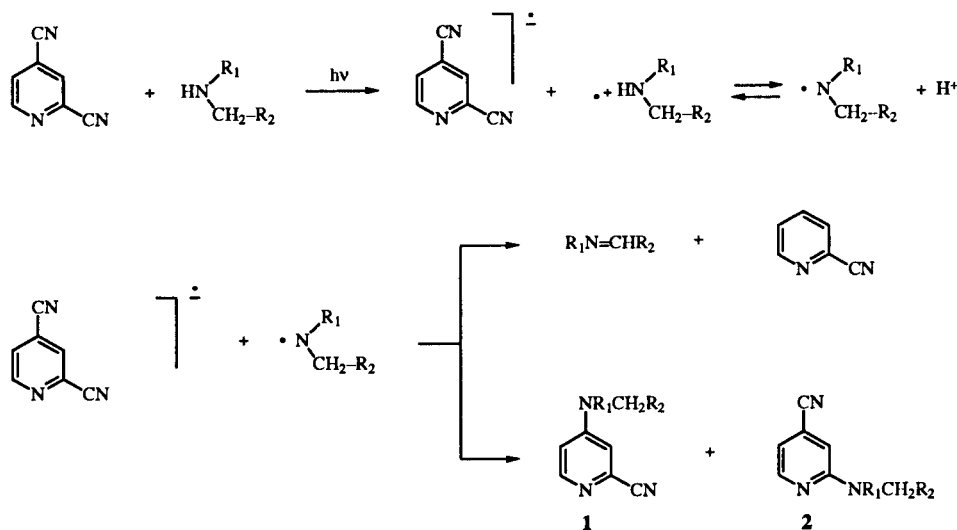
A study on the photochemically induced electron-transfer from primary and secondary aliphatic amines as donors to pyridinedicarbonitriles as the acceptor is reported. A comparison between the substitution positions and the spin density distributions, obtained *via* theoretical calculations using the 6-31+G basis set, shows some discrepancies, and forms the basis of a hypothesis on the mechanism of the reaction.

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Photochemically induced electron-transfer reactions have been a field of interest to the chemical community for a number of years. The areas of interest have included the thermodynamic implications relating to the transfer of an electron from a donor to an acceptor, the chemical behavior of the radical cation or the radical anion formed, and the synthetic interest of the final product. Some of this work has included the application of theoretical calculations in an attempt to obtain a better understanding of the effect of functional groups on the photochemical reactivity of these systems [1]. In our work, we have found pyridine-2,4-dicarbonitrile to be an excellent model compound as an electron acceptor, both in the ground state with ketyl radicals and in the excited state with alcohols, alkenes and aliphatic and aromatic amines [2]. In Scheme 1 is reported the proposed mechanism for this last reaction. Theoretical calculations at the 6-31G+ basis set level

indicate that position 4 of the 2,4-dicyanopyridinyl radical anion has a higher spin density than position 2. Consequently, one would expect that substitution should occur predominantly in position 4. Interestingly, this was found to be the case only for the amines with lower ionization potentials, while amines with higher ionization potentials gave a larger amount of substitution in the 2-position. We explained this observation by relating the position of substitution to the distance between the donor and the acceptor at the time of electron transfer. The closer the two are when the transfer occurs, the higher the possibility of substitution at position 2, while the farther apart the molecules are the greater the likelihood that substitution will occur at position 4. In order to test this hypothesis, and to explore the synthetic possibilities that might result, these studies were extended to the other dicyanopyridines substituted in the 2,3-, 2,5-, 2,6-, 3,4- and 3,5-positions.

Scheme 1



For these compounds theoretical calculations have been made utilizing the ROHF method with the 6-31+G basis set, considered the most suitable for the description of their negatively charged species [3].

Results and Discussion.

In Figure 1 are reported the result of spin density calculations for the dicyanopyridinyl radical anions corresponding to the compounds used in this study. In Figures 2-5 are reported the products obtained for each

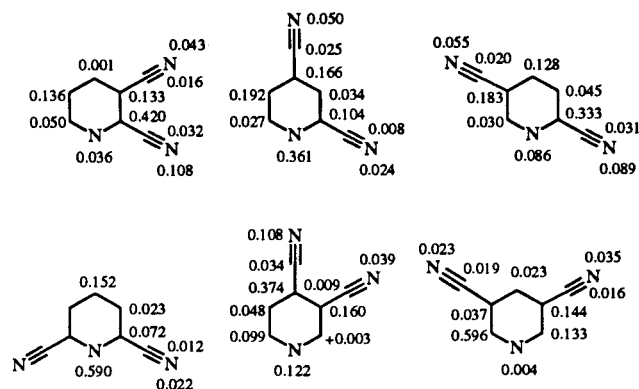


Figure 1. 6-31G+ *ab initio* calculations of the spin densities for the pyridinedicarbonitrile radical anions.

unless the C_{2v} symmetry is destroyed. This implies a degeneracy of two MO's competing for occupancy by the unpaired electron. No such problem is encountered for the other symmetric molecule, 2,6-pyridinedicarbonitrile.

As was found to be the case with 2,4-pyridinedicarbonitrile, the synthetic value of these reactions is also decreased due to the fact that a large amount of the mono cyanopyridine is obtained. Decyanation occurs because of the efficient hydrogen atom donor characteristic of the amine radical. As we reported earlier, a hydrogen atom is transferred to the 4 position of the dicyanopyridinyl radical anion resulting in the loss of the cyano from that position. The 2,5-isomer behaves differently in that a dimer is formed. We have found that most of the other dicyanopyridines also form dimers when other electron donors are used [4].

The only case in which substitution prevails is the reaction of *t*-butylamine, presumably because of the fact that no hydrogen is present on the carbon adjacent to the nitrogen atom. As for 2,4-pyridinedicarbonitrile, an examination of the product distribution shows an interesting dependence on the kind of amine used. There is a well defined difference between the reactivities of the primary and secondary amines. While with the secondary amines, the products are the ones that result from the substitution

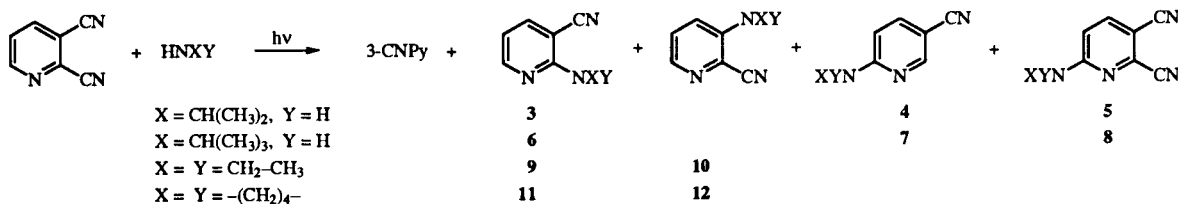


Figure 2

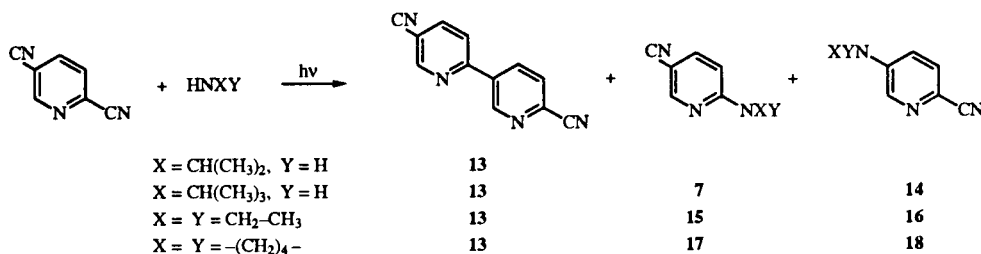


Figure 3

dicyanopyridine; the ratio between them, and the total yield are reported in Table 1. For the purpose of comparison, in the same Table are reported the corresponding values for 2,4-pyridinedicarbonitrile. The structural assignments and the physical properties are given in Table 2. The 3,5-dicyano isomer is not reported, since it is not reactive under our experimental conditions. For this compound no theoretical self consistent solution is reached

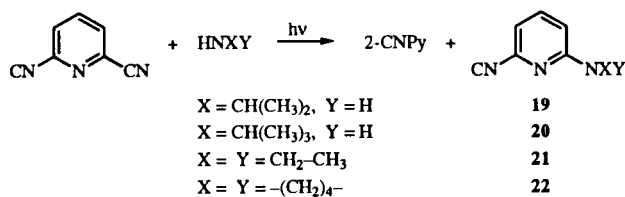


Figure 4

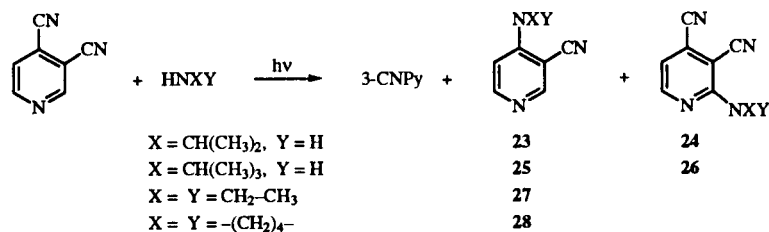


Figure 5

of the cyano group, in the case of the primary amines and, for example, 2,3- and 3,4-pyridinedicarbonitriles the products cannot be explained only with the mechanism proposed in Scheme 1. Even in the cases of the 2,4-, and 2,5-pyridinedicarbonitriles in which the products are predictable, the ratios are very different with the primary amines.

amine with a heterocyclic base could occur. These include the ionization potential of the amine as well as the reduction potential of the heterocycle, the spin density and charge distribution on the radical anion, and the orientation of the donor acceptor complex at the time of electron transfer. Immediately after the transfer, charge distribution becomes important. A reorientation of the radical

Table 1

Dicyanopyridine	Amine			
	Isopropyl	<i>t</i> -Butyl	Diethyl	Pyrrolidine
2,3-	$3/(4 + 5) = 0.2$ $5/4 = 8.0$	$6/(7 + 8) = 0.5$ $8/7 = 3.0$	$9/10 = 1.7$	$11/12 = 1.0$
Total Yield	$(3 + 4 + 5)/3\text{-CNPy} = 0.2$ 89%	$(6 + 7 + 8)/3\text{-CNPy} = 2.4$ 76%	$(9 + 10)/3\text{-CNPy} = 0.4$ 94%	$(11 + 12)/3\text{-CNPy} = 0.3$ 96%
2,5-		$7/14 = 6.1$	$15/16 = 1.4$	$17/18 = 1.3$
Total Yield	96%	$(7 + 14)/13 = 10.6$ 78%	$(15 + 16)/13 = 1.1$ 89%	$(17 + 18)/13 = 3.2$ 99%
2,6-	$19/2\text{-CNPy} = 0.2$	$20/2\text{-CNPy} = 1.0$	$21/2\text{-CNPy} = 0.3$	$22/2\text{-CNPy} = 0.4$
Total Yield	65%	50%	59%	72%
3,4-	$23/24 = 10.0$	$25/26 = 25.0$		
Total Yield	$(23 + 24)/3\text{-CNPy} = 0.2$ 90%	$(25 + 26)/3\text{-CNPy} = 3.3$ 41%	$27/3\text{-CNPy} = 0.1$ 71%	$28/3\text{-CNPy} = 0.1$ 67%
2,4-	$1/2 = 0.8$	$1/2 = 0.6$	$1/2 = 1.4$	$1/2 = 1.1$
Total Yield	$(1 + 2)/2\text{-CNPy} = 0.2$ 60%	$(1 + 2)/2\text{-CNPy} = 0.6$ 37%	$(1 + 2)/2\text{-CNPy} = 0.5$ 76%	$(1 + 2)/2\text{-CNPy} = 0.3$ 62%

In considering reactivity and mechanism regarding the photoreactions of primary and secondary amines with the various dicyanopyridines, it becomes clear there is no simple mechanism that explains all these reactions. However, there are various factors, one or more of which could influence how a photochemical reaction of an

cation and radical anion will occur to reflect this new charge distribution. Essentially all the reactions that we report here can be explained with one or more of these influencing factors. We have found that initially one of the most important factors is the ionization of the amine, assuming other things such as the reduction potential of the pyridine systems are nearly equal and appropriate for reaction. We reported earlier that if the amine has a lower ionization potential and the electron transfer requires relatively low energy, then the resulting radical ion pair would be relatively loose allowing for greater mobility of the ions.

Under these conditions, spin density distribution of the radical anion would become important and substitution should then be expected to occur at the positions of higher spin density. This was found to be the predominant way that secondary amines react with 2,3-, 2,4-, and 2,5-pyridinedicarbonitriles.

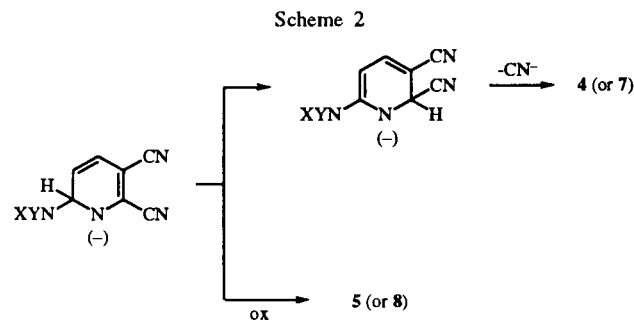


Table 2
Spectroscopic Data and Elemental Analyses of the Pyridine Derivatives

Product	Mp °C	Mass Spectra (m/z)	¹ H NMR δ [a]	Molecular Formula	Calcd./Found%		
					C	H	N
3	oil	161, 146, 119, 103	8.23 (dd, 1H, H _A , J _{A-B} = 5 Hz, J _{A-C} = 1 Hz), 7.60 (dd, 1H, H _C , J _{C-B} = 8 Hz, J _{C-A} = 1 Hz), 6.50 (dd, 1H, H _B , J _{B-A} = 5 Hz, J _{B-C} = 8 Hz), 4.90 (m, 1H, NH), 4.31 (m, 1H, CH(CH ₃) ₂ , J ₁₋₂ = 7 Hz), 1.28 (d, 6H, 2 CH ₃ , J ₂₋₁ = 7 Hz)	C ₉ H ₁₁ N ₃	67.05 66.97	6.88 6.89	26.07 26.13
4	90-95	161, 146, 119, 103, 92	8.30 (d, 1H, H _A , J _{A-C} = 2 Hz), 7.51 (dd, 1H, H _C , J _{C-A} = 2 Hz, J _{C-D} = 9 Hz), 6.28 (d, 1H, H _D , J _{D-C} = 9 Hz), 4.81 (m, 2H, NH, and CH(CH ₃) ₂ , J ₁₋₂ = 7 Hz), 1.22 (d, 6H, 2 CH ₃ , J ₂₋₁ = 7 Hz)	C ₉ H ₁₁ N ₃	67.05 66.99	6.88 6.88	26.07 26.13
5	156-159	186, 172, 171, 144, 128, 117	7.59 (d, 1H, H _B , J _{B-C} = 9 Hz), 6.51 (d, 1H, H _C , J _{C-B} = 9 Hz), 5.27 (m, 1H, NH), 4.10 (m, 1H, CH(CH ₃) ₂ , J ₁₋₂ = 6 Hz), 1.30 (d, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₁₀ H ₁₀ N ₄	64.50 64.58	5.41 5.41	30.09 30.02
6	oil	175, 160, 115, 92	8.23 (dd, 1H, H _A , J _{A-B} = 5 Hz, J _{A-C} = 2 Hz), 7.57 (dd, 1H, H _C , J _{C-B} = 8 Hz, J _{C-A} = 2 Hz), 6.49 (dd, 1H, H _B , J _{B-A} = 5 Hz, J _{B-C} = 8 Hz), 5.05 (bs, 1H, NH), 1.45 (s, 9H, 3 CH ₃)	C ₁₀ H ₁₃ N ₃	68.54 68.47	7.48 7.48	23.98 24.05
7	104-107	175, 160, 119, 103	8.30 (d, 1H, H _A , J _{A-C} = 2 Hz), 7.45 (dd, 1H, H _C , J _{C-A} = 2 Hz, J _{C-D} = 9 Hz), 6.31 (d, 1H, H _D , J _{D-C} = 9 Hz), 4.92 (bs, 1H, NH), 1.46 (s, 9H, 3 CH ₃)	C ₁₀ H ₁₃ N ₃	68.54 68.80	7.48 7.46	23.98 23.74
8	135-140	200, 185, 145, 144, 128	7.53 (d, 1H, H _B , J _{B-C} = 9 Hz), 6.60 (d, 1H, H _C , J _{C-B} = 9 Hz), 5.41 (bs, 1H, NH), 1.46 (s, 9H, 3 CH ₃)	C ₁₁ H ₁₂ N ₄	65.98 66.22	6.04 6.04	27.98 27.74
9	oil	175, 160, 146, 132, 105, 103	8.29 (dd, 1H, H _A , J _{A-B} = 6 Hz, J _{A-C} = 2 Hz), 7.69 (dd, 1H, H _C , J _{C-B} = 9 Hz, J _{C-A} = 2 Hz), 6.50 (dd, 1H, H _B , J _{B-A} = 6 Hz, J _{B-C} = 9 Hz), 3.74 (q, 4H, 2 CH ₂ -N, J ₁₋₂ = 8 Hz), 1.29 (t, 6H, 2 CH ₃ , J ₂₋₁ = 8 Hz)	C ₁₀ H ₁₃ N ₃	68.54 68.37	7.48 7.47	23.98 24.16
10	oil	175, 160, 132, 105	8.10 (dd, 1H, H _A , J _{A-B} = 3 Hz, J _{A-C} = 1 Hz), 7.30 (m, 2H, H _B and H _C), 3.49 (q, 4H, 2 CH ₂ -N, J ₁₋₂ = 8 Hz), 1.20 (t, 6H, 2 CH ₃ , J ₂₋₁ = 8 Hz)	C ₁₀ H ₁₃ N ₃	68.54 68.70	7.48 7.45	23.98 23.85
11	60-65	173, 144, 118, 103	8.22 (dd, 1H, H _A , J _{A-B} = 5 Hz, J _{A-C} = 2 Hz), 7.63 (dd, 1H, H _C , J _{C-B} = 7 Hz, J _{C-A} = 2 Hz), 6.49 (dd, 1H, H _B , J _{B-A} = 5 Hz, J _{B-C} = 7 Hz), 3.73 (m, 4H, CH ₂ -N-CH ₂), 2.00 (m, 4H, CH ₂ -CH ₂)	C ₁₀ H ₁₁ N ₃	69.34 69.27	6.40 6.41	24.26 24.32
12	oil	173, 172, 145, 104, 83	7.96 (dd, 1H, H _A , J _{A-B} = 4 Hz, J _{A-C} = 1 Hz), 7.22 (dd, 1H, H _B , J _{B-A} = 4 Hz, J _{B-C} = 9 Hz), 6.98 (dd, 1H, H _C , J _{C-A} = 1 Hz, J _{C-B} = 9 Hz), 3.60 (m, 4H, CH ₂ -N-CH ₂), 2.08 (m, 4H, CH ₂ -CH ₂)	C ₁₀ H ₁₁ N ₃	69.34 69.07	6.40 6.42	24.26 24.51
13	202-205	206, 205, 180, 103	9.39 (d, 1H, H _A , J _{A-C} = 2 Hz), 8.99 (m, 2H, H _D and H _{A'} , J _{D-C} = 5 Hz, J _{A'-C} = 1 Hz), 8.78 (dd, 1H, H _C , J _{C-A} = 2 Hz, J _{C-D} = 5 Hz), 8.12 (dd, 1H, H _C , J _{C-A} = 1 Hz, J _{C-D} = 7 Hz), 7.91 (d, 1H, H _{D'} , J _{D'-C} = 7 Hz)	C ₁₂ H ₆ N ₄	69.90 69.91	2.93 2.93	27.17 27.16
14	78-82	175, 160, 119, 103, 91	7.99 (d, 1H, H _A , J _{A-C} = 3 Hz), 7.40 (d, 1H, H _D , J _{D-C} = 9 Hz), 6.88 (dd, 1H, H _C , J _{C-D} = 9 Hz, J _{C-A} = 3 Hz), 4.28 (bs, 1H, NH), 1.41 (s, 9H, 3 CH ₃)	C ₁₀ H ₁₃ N ₃	68.54 68.32	7.48 7.46	23.98 24.22
15	oil	175, 160, 146, 132, 103	8.36 (d, 1H, H _A , J _{A-C} = 2 Hz), 7.52 (dd, 1H, H _C , J _{C-A} = 2 Hz, J _{C-D} = 9 Hz), 6.41 (d, 1H, H _D , J _{D-C} = 9 Hz), 3.55 (q, 4H, CH ₂ -N-CH ₂ , J ₁₋₂ = 6 Hz), 1.20 (t, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₁₀ H ₁₃ N ₃	68.54 68.52	7.48 7.49	23.98 23.98
16	oil	175, 160, 132, 119	8.08 (d, 1H, H _A , J _{A-C} = 3 Hz), 7.42 (d, 1H, H _D , J _{D-C} = 8 Hz), 6.81 (dd, 1H, H _C , J _{C-D} = 8 Hz, J _{C-A} = 3 Hz), 3.42 (q, 4H, CH ₂ -N-CH ₂ , J ₁₋₂ = 6 Hz), 1.20 (t, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₁₀ H ₁₃ N ₃	68.54 68.67	7.48 7.47	23.98 23.86
17	54-58	173, 145, 144, 118, 104, 103	8.36 (d, 1H, H _A , J _{A-C} = 1 Hz), 7.51 (dd, 1H, H _C , J _{C-A} = 1 Hz, J _{C-D} = 9 Hz), 6.29 (d, 1H, H _D , J _{D-C} = 9 Hz), 3.40 (m, 4H, CH ₂ -N-CH ₂), 2.00 (m, 4H, CH ₂ -CH ₂)	C ₁₀ H ₁₁ N ₃	69.34 69.27	6.40 6.42	24.26 24.31
18	65-70	173, 172, 144, 130, 117, 103	7.98 (d, 1H, H _A , J _{A-C} = 2 Hz), 7.40 (d, 1H, H _D , J _{D-C} = 8 Hz), 6.69 (dd, 1H, H _C , J _{C-D} = 8 Hz, J _{C-A} = 2 Hz), 3.38 (m, 4H, CH ₂ -N-CH ₂), 2.00 (m, 4H, CH ₂ -CH ₂)	C ₁₀ H ₁₁ N ₃	69.34 69.50	6.40 6.39	24.26 24.11

Table 2 (continued)

Product	Mp °C	Mass Spectra (m/z)	¹ H NMR δ [a]	Molecular Formula	Calcd./Found%		
					C	H	N
19	oil	161, 146, 119	7.38 (dd, 1H, H _C , J _{C-B} = 8 Hz, J _{C-D} = 9 Hz), 6.87 (d, 1H, H _B , J _{B-C} = 8 Hz), 6.49 (d, 1H, H _D , J _{D-C} = 9 Hz), 4.51 (bs, 1H, NH), 3.98 (m, 1H, NH-CH, J ₁₋₂ = 6 Hz), 1.15 (t, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₉ H ₁₁ N ₃	67.05 67.10	6.88 6.86	26.07 26.04
20	oil	175, 160, 120, 119, 92	7.33 (dd, 1H, H _C , J _{C-B} = 8 Hz, J _{C-D} = 9 Hz), 6.87 (d, 1H, H _B , J _{B-C} = 8 Hz), 6.48 (d, 1H, H _D , J _{D-C} = 9 Hz), 4.58 (bs, 1H, NH), 1.45 (s, 9H, 3 CH ₃)	C ₁₀ H ₁₃ N ₃	68.54 68.31	7.48 7.51	23.98 24.18
21	100-102	175, 160, 146, 132, 103	7.37 (dd, 1H, H _C , J _{C-B} = 8 Hz, J _{C-D} = 9 Hz), 6.80 (d, 1H, H _B , J _{B-C} = 8 Hz), 6.51 (d, 1H, H _D , J _{D-C} = 9 Hz), 3.49 (q, 4H, CH ₂ -N-CH ₂ , J ₁₋₂ = 7 Hz), 1.12 (t, 6H, 2 CH ₃ , J ₂₋₁ = 7 Hz)	C ₁₀ H ₁₃ N ₃	68.54 68.50	7.48 7.46	23.98 24.04
22	oil	173, 144, 104, 103	7.40 (dd, 1H, H _C , J _{C-B} = 8 Hz, J _{C-D} = 9 Hz), 6.83 (d, 1H, H _B , J _{B-C} = 8 Hz), 6.48 (d, 1H, H _D , J _{D-C} = 9 Hz), 3.41 (m, 4H, CH ₂ -N-CH ₂), 1.98 (m, 4H, CH ₂ -CH ₂)	C ₁₀ H ₁₁ N ₃	69.34 69.13	6.40 6.40	24.26 24.47
23	oil	161, 146, 119, 92	8.47 (s, 1H, H _E), 8.34 (d, 1H, H _A , J _{A-B} = 6 Hz), 6.55 (d, 1H, H _B , J _{B-A} = 6 Hz), 4.88 (bs, 1H, NH), 3.80 (m, 1H, NH-CH, J ₁₋₂ = 6 Hz), 1.33 (t, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₉ H ₁₁ N ₃	67.05 67.26	6.88 6.86	26.07 25.88
24	50-55	186, 171, 144, 117, 103	8.44 (s, 1H, H _A , J _{A-B} = 6 Hz), 6.80 (d, 1H, H _B , J _{B-A} = 6 Hz), 5.21 (bs, 1H, NH), 4.31 (m, 1H, NH-CH, J ₁₋₂ = 6 Hz), 1.30 (t, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₁₀ H ₁₀ N ₄	64.50 64.25	5.41 5.42	30.09 30.33
25	oil	175, 160, 129, 120, 119, 102	8.51 (s, 1H, H _E), 8.36 (d, 1H, H _A , J _{A-B} = 6 Hz), 6.84 (d, 1H, H _B , J _{B-A} = 6 Hz), 5.05 (bs, 1H, NH), 1.50 (s, 9H, 3 CH ₃)	C ₁₀ H ₁₃ N ₃	68.54 68.77	7.48 7.49	23.98 23.74
26	oil	200, 185, 170, 145, 144, 128	8.47 (s, 1H, H _A , J _{A-B} = 6 Hz), 6.82 (d, 1H, H _B , J _{B-A} = 6 Hz), 5.37 (bs, 1H, NH), 1.51 (s, 9H, 3 CH ₃)	C ₁₁ H ₁₂ N ₄	65.98 65.85	6.04 6.06	27.98 28.09
27	oil	175, 160, 132	8.55 (s, 1H, H _E), 8.29 (d, 1H, H _A , J _{A-B} = 6 Hz), 6.60 (d, 1H, H _B , J _{B-A} = 6 Hz), 3.67 (q, 4H, CH ₂ -N-CH ₂ , J ₁₋₂ = 6 Hz), 1.33 (t, 6H, 2 CH ₃ , J ₂₋₁ = 6 Hz)	C ₁₀ H ₁₃ N ₃	68.54 68.41	7.48 7.48	23.98 24.11
28	oil	173, 172, 145, 118, 104	8.40 (s, 1H, H _E), 8.18 (d, 1H, H _A , J _{A-B} = 6 Hz), 6.39 (d, 1H, H _B , J _{B-A} = 6 Hz), 3.47 (m, 4H, CH ₂ -N-CH ₂), 2.05 (m, 4H, CH ₂ -CH ₂)	C ₁₀ H ₁₁ N ₃	69.34 69.33	6.40 6.42	24.26 24.25

[a] For solutions in deuteriochloroform, all coupling constants (J) are in Hz. H_A, H_B, H_C, H_D, and H_E refer respectively to the protons in positions 6, 5, 4, 3, 2 of the pyridine ring. For the other J values, the numbers refer to the carbon atoms of the amine, starting from the one attached to the nitrogen.

The reactions of the primary amines can be explained using a similar argument. Primary amines generally have a higher ionization potential than secondary amines. It would be expected, therefore, that the radical ion complex formed from these amines should be tighter than that from secondary amines. After electron transfer occurs, it would be expected that substantial charge density would develop on the ring nitrogen. If electron transfer occurs along the π -system of the heterocyclic ring anywhere near the ring nitrogen, the radical cation would be driven closer to that nitrogen atom and would be close to the 2 and 6 positions of the ring where cross-coupling could then occur. Migration of the radical cation to another side of the radical anion results in the formation of the other products observed. This mechanism would help explain why with primary amines substitution occurs at position 2 rather than 4 for the second though calculations indicate that for the 2,4-isomer, the spin density should be higher at position 4; the same applies to the latter compound for

which the ratio of substitution between position 2 and 5 for *t*-butylamine is much larger than those of the secondary amines.

This mechanism also explains why in the case of reactions with primary amines substitution occurs at the 2 and the 4 position of the 3,4-isomer even though the 2 position bears no cyano groups. In the case of the 2,3-isomer, substitution occurs at both 2 and 6 positions with primary amines. When the 6 position is attacked, the cyano group in the 2 position may be eliminated. We postulate that this could occur through a [1,5] sigmatropic shift of hydrogen, which is thermally allowed suprafacially, followed by elimination of the cyano group.

In contrast to the photoreactions of the primary amines, the secondary amines would be expected to transfer their electron at a greater distance than do primary amines and form looser charge transfer complexes. The resulting radical cations may probably transfer the proton to the solvent cage and can then easily move to positions of highest spin

density of the heterocyclic ring and couple at those positions. The products obtained with the various dicyanopyridines reflects this process.

In conclusion, this work shows a method by which aminopyridines can be conveniently synthesized and demonstrates the sensitivity of the position of substitution to the ionization potential of the donor molecule and to the energy of the electron transfer process.

EXPERIMENTAL

All amines were freshly distilled before use. 3,4-Pyridinedicarbonitrile was purchased from the Aldrich Chemical Company and recrystallized once from ethanol. The 2,3-, 2,5-, 2,6-, and 3,5-pyridinedicarbonitriles were synthesized from the corresponding pyridinedicarboxylic acids according to procedures described by Skala and Kuthan [5] and purified by column chromatography on silica gel. Solid products obtained from column chromatography were sufficiently pure and were not purified further. Melting points are uncorrected. The nmr spectra were recorded on a Varian EM 390 90 MHz spectrometer and chemical shifts are reported in ppm (δ) relative to TMS as the internal standard, J values are given in Hz, the solvent was deuteriochloroform. Mass spectra were recorded with a Hitachi-Perkin Elmer RMU 6D single focusing spectrometer. Gas chromatographic analyses were performed on a Dani 3800 gas chromatograph using a 2 m glass column (i.d. 2 mm) packed with 5% SP-1000 on 100/200 Supelcoport at 220° or a 2 m glass column (i.d. 2 mm) packed with 10% UCC-W 982 on chrm. W-AW-DMSC and temperature programmed from 120° to 235° (8°/minute after the first 4 minutes) using a flame ionization detector. A mixture of weighted compounds and standard was used to calibrate the detector response and peak areas were used to determine the product ratios.

All the photochemical reactions were run in quartz vessels in a RPR-100 Rayonet photochemical reactor equipped with 16 low-pressure mercury lamps. Irradiation was carried out for a period of 4 hours at 254 nm with deaerated solutions. In a typical experiment the heterocycle (1 mmole) was dissolved in acetonitrile (20 ml) and the appropriate amine (5 mmoles) was added. After irradiation, the solvent was removed under reduced pressure, and the resulting mixture was either analyzed by glc or separated by standard flash chromatography [6] on Merck silica gel (0.040-0.063 mesh) using different mixtures of hexane-ethyl

acetate. The physical properties and the spectroscopic data are reported in Table 2.

Theoretical calculations at the 6-31+G level were performed using the software Gaussian 92 [7], the geometry was optimized assuming a planar structure.

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