An Electron Spin Resonance and Voltammetric Investigation of Some 2-Mono- and 2,4-Di-substituted Pyridinyl Radicals

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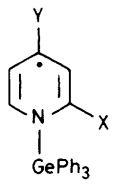
The chemical reduction of some 2-monosubstituted and 2,4-disubstituted pyridinium ions has been investigated by means of e.s.r. spectroscopy and the results compared with those of an electrochemical study on the same species. By combining the electrochemical and e.s.r. data, a scale of stability has been determined for the investigated pyridinyl radicals. *N*-Methyl-2-cyanopyridinyl, which was found to be too unstable to be observed, eventually evolved to the 2,4-dicyano-substituted radical. E.s.r. studies have also been carried out on the structurally similar, although more persistent, *N*-germylpyridinyls.

Since Kosower and Poziomek's report of the detection of the 1-ethyl-4-methoxycarbonylpyridinyl radical,[1] pyridinyls have been the subject of several investigations,[2–4] and their stability has been found to be strongly dependent on the nature and ring position of the substituents.[5] These paramagnetic species can be generated by a variety of methods,[6] which include chemical and electrochemical[7] reduction of pyridinium cations, thermolysis, and pulse radiolysis of the related dimers. Moreover, pyridinyls can be obtained by addition of Group IV organometallic radicals to substituted pyridines under suitable experimental conditions.[8]

Previous polarographic work has shown that 2-cyano-*N*-methylpyridinium salts[9] exhibit, in an aqueous medium, a behaviour that differs drastically from that of the 3-cyano[10] and 4-cyano[11] isomers. Moreover, from recent experiments it would also appear that in non-aqueous media (DMF, ACN, and DMSO) the electrochemical behaviour of the 2-cyano derivative differs from that of other pyridinium salts containing strong acceptor groups such as $-CO_2R$ in position 2.[12] Since in preliminary e.s.r. studies we noticed that reduction of 2-cyano-1-methylpyridinium iodide, as opposed to the 4-cyano isomer, leads to confusing spectra, which indicate the simultaneous presence of more than one radical species, we undertook an e.s.r. and polarographic investigation of a few 2- and 2,4-substituted pyridinium salts in order to try and rationalize their behaviour towards chemical and electrochemical reduction. We report here the results obtained for pyridinyls (**2a**—**f**) generated from the corresponding salts (**4a**—**f**). To obtain further information on these species we also studied the related 1-germylpyridinyls (**1a**—**f**) by e.s.r., produced by addition of *in situ* generated triphenylgermyl radicals to the free bases (**3a**—**f**).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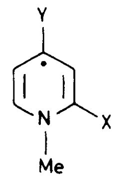
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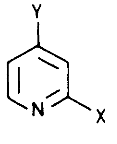
a; X = CN, Y = H
b; X = CN, Y = Me
c; X = CN, Y = Bu^t
d; X = CO_2Et, Y = H
e; X = COMe, Y = H
f; X = Y = CN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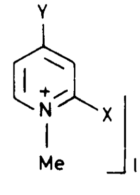
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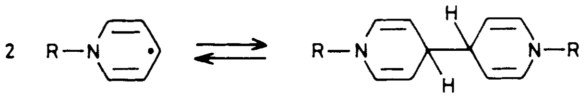
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Results and Discussion

N-*Triphenylgermylpyridinyls.*—Germyl radicals readily add to the heterocyclic nitrogen of pyridines (**3a**—**f**) to give the corresponding pyridinyl radicals (**1a**—**f**), with the exception of 2-acetylpyridine (**3e**), which gives a very weak and uninterpretable signal. The intensity of the e.s.r. spectrum is normally enhanced by increasing the temperature: thus most spectra were recorded at *ca.* 60 °C, and in the case of the 2-CN adduct (**1a**) temperatures as high as 130 °C were needed to obtain a satisfactory signal-to-noise ratio. This is in line with the well known tendency of pyridinyl radicals to undergo recombination and give diamagnetic dimers according to equilibrium (i).

The introduction of a substituent in the 4-position will make the approach of the two radical moieties more difficult, disfavouring the dimerization process and allowing the detection of the radical adducts at lower temperatures. The importance of the effects exerted by electron-withdrawing substituents in stabilizing the monomeric pyridinyls has been stressed previously.[3,4] It should be expected that in equilibrium (i) the formation of the dimer is favoured for pyridinyls having large

Table 1. Hyperfine splitting constants (G) for radicals (**1**) and (**2**)

Radical	Solvent[a]	a_N	a_{H-3}	a_{H-5}	a_{H-6}	a_{X-2}	a_{Y-4}	a_{N-Me}	g
(**1a**)	BB	5.43	2.16	1.23	2.47	1.73 (1 N)	8.19 (1 H)		
(**1b**)	BB	4.93	1.84	1.54	2.03	1.92 (1 N)	8.0 (3 H)		
(**1c**)	BB	5.07	1.83	1.71	1.91	1.91 (1 N)			2.0028
(**1d**)	BB	5.31	1.64	1.57	2.17	3.0 (2 H, Et)	6.86 (1 H)		2.0032
(**1f**)	BB	7.10	2.26	1.89	3.79	1.38 (1 N)	1.95 (1 N)		2.0030
(**2c**)	DMSO	6.90	1.34	1.34	2.40	1.20 (1 N)	0.14 (9 H)	5.84	2.0028
(**2e**)	DMSO	5.44	0.74	0.46	2.82	3.0 (3 H)	4.72 (1 H)	5.06	
(**2f**)	DMSO	7.30	0.79	0.60	1.35	0.73 (1 N)	1.27 (1 N)	6.55	

[a] BB = t-butylbenzene; DMSO = dimethyl sulphoxide.

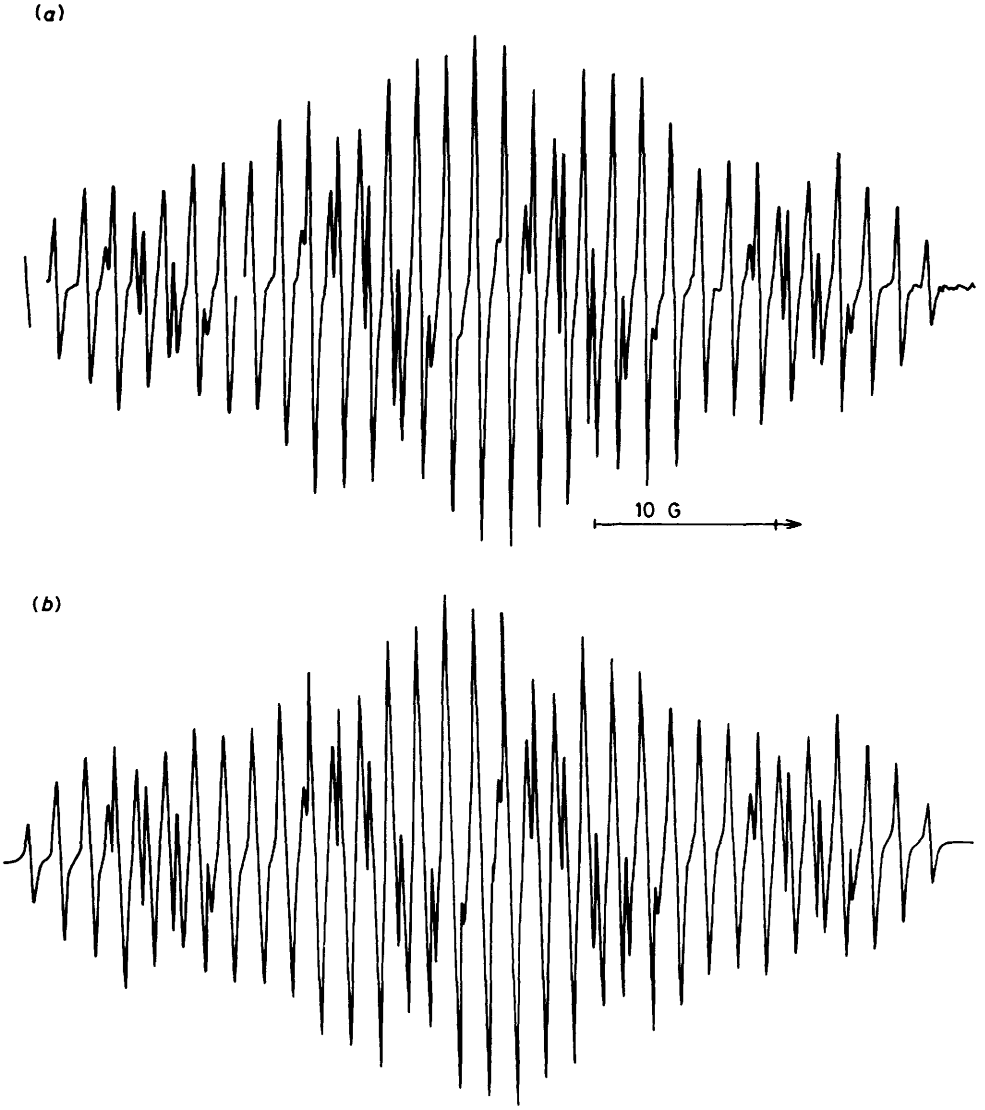


Figure 1. Experimental (*a*) and simulated (*b*) e.s.r. spectra of (**4d**)

spin densities in the 4-position. In this respect, it is not surprising that radical (**1d**), which exhibits a coupling constant for the hydrogen in this position significantly smaller than that measured for (**1a**), could be observed under less drastic experimental conditions.

It is also worth noting the stabilizing role played by the entering organometallic group. In the 1-alkylpyridinyls carrying no substituents at the 4-position, the monomer–dimer equilibrium is completely shifted to the right,[4] even if electron-withdrawing substituents are present in the other positions of the molecule, with the exception of 1-methyl-2-acetyl- and 1-methyl-2-methoxycarbonyl-pyridinyl. However, the 2-substituted-1-trialkylsilyl- and 1-trialkylgermyl-pyridinyl radicals can be detected by e.s.r. The lower π-electron-accepting ability, which is characteristic of germanium compared with silicon, does not allow detection of the unsubstituted 1-trialkylgermylpyridinyl radical.[13]

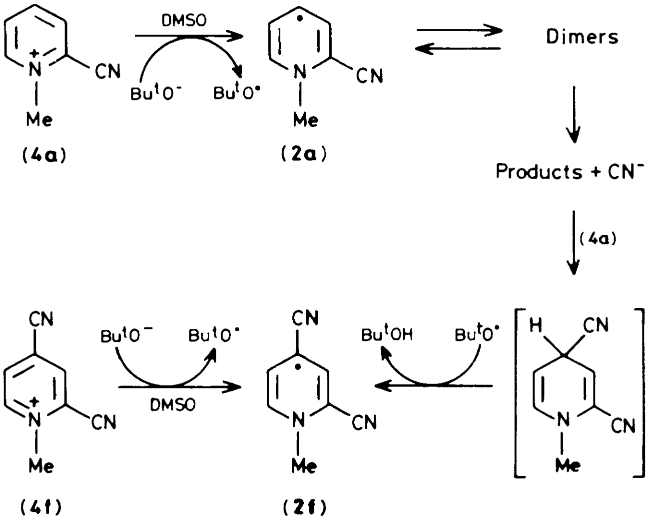
The e.s.r. parameters for radicals (**1a**—**d**) and (**1f**) are collected in Table 1. All spectra indicated coupling of the unpaired electron with the heterocyclic nitrogen, four or three aromatic protons, and the nitrogen atom of the cyano group, the latter splitting being substituted in (**1d**) by a 1:2:1 triplet from the methylene protons of the ethoxycarbonyl group (Figure 1). The doublet splitting of the *para*-proton changed into a 1:3:3:1 quartet in (**1b**), whereas coupling from the butyl protons in (**1c**) could not be resolved. Assignment of the couplings to the different positions was made by comparison with previously reported data for the 2-cyano-1-hydropyridinyl[14] and 2-methoxycarbonyl-1-methylpyridinyl[5,15] radicals. There is, however, some ambiguity as far as the assignment of the two smaller proton splittings is concerned, although McLachlan MO calculations* suggest that the 3-position should be characterized by a slightly larger spin density with respect to the 5-position.

At variance with what was found for the above mentioned pyridines (**3a**—**d**) and (**3f**), the reaction of triphenylgermyl radicals with 2-acetylpyridine (**3e**) over a wide temperature range poses problems, as only a very weak signal could be observed which we were unable to interpret. Our failure to detect the expected radical adduct (**1e**) is peculiar because of the presence of the acetyl group in position 2, which should exert a strong stabilizing action. It is, however, possible that steric requirements in the germyl adduct push the acetyl group well out of the plane of the π-system, if it is not in an arrangement orthogonal to it, thus minimizing its stabilizing effect. Although possible in principle, the occurrence of a competitive addition reaction of the germyl radical to the carbonyl group should be discarded, as it is known that group IVB organometallic radicals ($\dot{S}iR_3$ and $\dot{G}eR_3$) attack the nitrogen of 4-acetylpyridine rather than the oxygen of its carbonyl group.[8]

N-*Methylpyridinyls.*—*A. Reduction of* (**4a**—**e**) *with* Bu^{t}OK. As already mentioned in the preceding section, *N*-alkylpyridinyls are much less persistent species than their *N*-germyl analogues. On chemical reduction of the corresponding pyridinium salts, we could unambiguously identify only 2-cyano-4-t-butyl-*N*-methylpyridinyl (**2c**) in addition to the already known 2-acetyl derivative (**2e**).[5]

The fact that we were able to detect this last species, whereas we could not observe the germyl analogue (**1e**), suggests that in the 1-methyl derivative the steric hindrance is less drastic and that the acetyl group does not deviate from coplanarity with the π-system to a great extent. However, observation of (**2c**) is presumably due to the combined effect of the cyano group in the 2-position (stabilization due to delocalization of the unpaired electron) and of the t-butyl group in the 4-position (disfavoured dimerization due to steric hindrance).

No clearly identifiable radicals could be observed in the chemical reduction of pyridinium salts (**4b**) and (**4d**): in all cases at least two paramagnetic species were simultaneously present and the spectral pattern kept changing in time with rates that appeared to depend on the relative concentrations of the salts and the reducing agent. Our failure to detect a clean e.s.r. spectrum attributable to (**2d**) upon chemical reduction of the salt (**4d**) is disconcerting in the light of the fact that the e.s.r. detection of the analogous 2-methoxycarbonyl-*N*-methylpyridinyl has been previously reported.[5] In our opinion this can be attributed to a different conformational preference of the alkoxycarbonyl group in the two cases, and/or to the different experimental techniques used in the present investigation.



Scheme 1.

Table 2. Polarographic data for the reduction of methylpyridinium cations (**4a**—**e**) in DMF[a]

Compound	First wave			Second wave		Third wave	
	$-E_{1/2}$/V	i_1/μA	I	$-E_{1/2}$/V	i_1/μA	$-E_{1/2}$/V	i_1/μA
(**4a**)	0.66	0.98	1.6	1.29	0.34	1.72	0.64
(**4b**)	0.78	0.96	1.6	1.36	0.51	1.72	0.94
(**4c**)	0.78	0.97	1.7	1.39	0.42	1.79	0.99
(**4d**)	0.84	1.20	2.1	1.60	0.30		
(**4e**)	0.78	1.18	2.1	1.45	1.16		

[a] The polarograms were recorded by the d.c.-sampled technique. Solutions were DMF–Bu_4NClO_4 0.1M, reactant *ca.* 1.5 × 10^{-3}M. The potentials are referred to Hg–Hg_2Cl_2, $NaCl_{(sat.aq.)}$ in DMF.[16] $I = i_1 m^{2/3} t^{1/6}$mM; T = 20.0 °C.

The salt (**4a**) deserves more detailed comment as, although on reduction it showed a behaviour similar in many respects to that of (**4b**) and (**4d**), after a long period of time it exhibited a clean e.s.r. spectrum, which was identical with that obtained by reduction of the 2,4-dicyano-1-methylpyridinium ion (**4f**). The formation of (**2f**) indicates the presence of cyanide anions in solution, in agreement with the polarographic data (*vide infra*). The mechanism leading to the dicyano-substituted radical (**2f**) is as yet unclear, but it seems reasonable that the CN$^-$ anions originate through decomposition of the first formed dimeric species and we believe that the reaction sequence leading to (**2f**) can be tentatively explained by Scheme 1.

In the absence of experimental evidence, we suggest that a possible dimer undergoing loss of the cyanide anion is 1,1′-dimethyl-2,2′-dicyano-1,1′,2,4′-tetrahydro-2,4′-bipyridine, as already hypothesized in previous work.[9]

B. Electrochemical reduction of (**4a**—**e**). The pyridinium salts (**4a**—**e**) have been examined from an electrochemical point of view in order to test the stability of the primary one-electron reduction products.

In DMF, with Bu_4NClO_4 as the supporting electrolyte and with a cathodic potential span up to −2.0 V, they exhibit two, (**4d**) and (**4e**), or three, (**4a**—**c**), subsequent steps. Typical normal-pulse (NP) polarographic curves are reported in Figures 2—4 and direct current polarographic data are reported in Table 2.

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* The following set of parameters has been used: $h_{\dot{N}} = 1.5$, $h_{\dot{N}-CN} = 1.0$, $K_{CC} = 1.0$, $K_{C-CN} = 0.9$, and $K_{CN} = 2.0$.

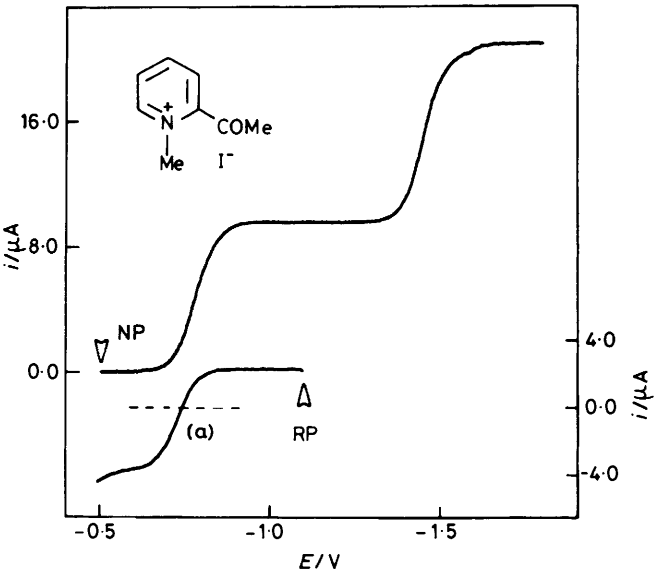


Figure 2. Normal pulse (NP) and reverse pulse (RP) waves for 3.0×10^{-3}M pyridinium iodide (**4e**) in DMF with 0.1M Bu_4NClO_4. Arrows indicate the initial potential

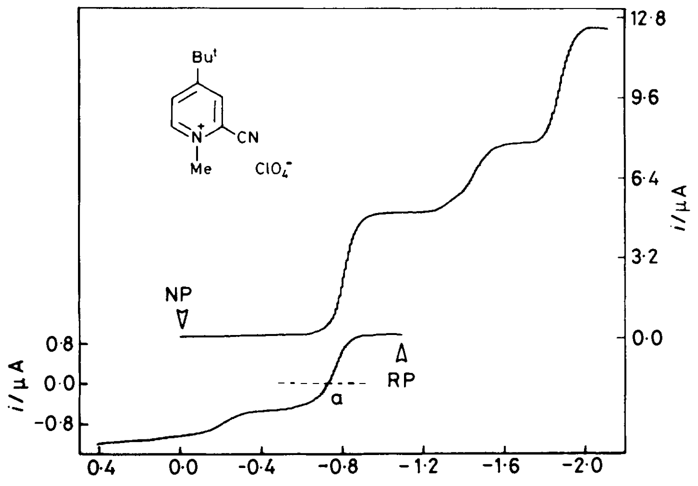


Figure 3. Normal pulse (NP) and reverse pulse (RP) waves for 2.0×10^{-3}M pyridinium perchlorate (**4c**) in DMF with 0.1M Bu_4NClO_4. Arrows indicate the initial potential

Reduction of the 2-acetylpyridinium cation (**4e**) under polarographic conditions yields a one-electron reversible step with formation of the corresponding radical (**2e**). The stability of radical (**2e**) is confirmed by observation of its oxidation step [anodic wave (a) in Figure 2] in reverse-pulse (RP) polarography.[17]

The reversibility of the charge transfer was also proved by cyclic voltammetric experiments, which led to voltammograms exhibiting an anodic–cathodic system, which, even at the lower sweep rate used (50 mV s^{-1}), is typical of a one-electron reversible process producing a species that is stable over the time interval necessary for the measurements.[18]

The electrochemical behaviour of the 2-ethoxycarbonyl-1-methylpyridinium cation (**4d**) is similar to that reported for the analogous 2-methoxycarbonyl-1-methylpyridinium salt.[12]

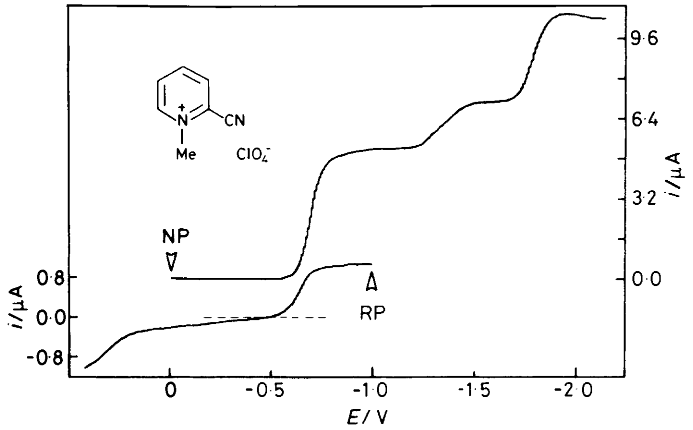


Figure 4. Normal pulse (NP) and reverse pulse (RP) waves for 2.1×10^{-3}M pyridinium perchlorate (**4a**) in DMF with 0.1M Bu_4NClO_4. Arrows indicate the initial potential

However, at variance with (**4e**), the reverse-pulse polarographic technique shows that under our experimental conditions the formation of radical (**2d**) is followed by a very rapid dimerization. In fact, the corresponding RP curves exhibit a very small anodic wave (a) followed by a substantial second anodic wave (at about 0.0 V) attributable to a dimeric species.[12] The instability of radical (**2d**) is also proved by cyclic voltammetric measurements. In fact, the voltammograms recorded at a sweep rate of 0.05—100 V s^{-1} show a small anodic peak (i_{p_a}) complementary with the cathodic peak (i_{p_c}), which, even though increasing with the sweep rate, is nevertheless always smaller than i_{p_c}.

A comparison of the first reduction step of the 2-cyano derivatives (**4a**—**c**) with the corresponding step of the 2-ethoxycarbonyl (**4d**) and 2-acetyl (**4e**) derivatives indicates that the diffusion current constant values (*I*, Table 2) obtained for (**4a**—**c**) are lower than those calculated for the cations (**4d**) and (**4e**), *i.e.*, in the first reduction step of the 2-cyano derivatives (**4a**—**c**) less than one electron per molecule of the substrate is involved.

An explanation of such an anomalous behaviour, which appears to be independent of the medium used (DMF, DMSO, ACN, *etc.*), may be related to follow-up chemical reactions of the primary one-electron reduction products involving the starting cations. It is important to note that when increasing amounts of protonating agents as strong as benzoic or monochloroacetic acid are added to the pyridinium salt solutions, the first reduction steps of the 2-ethoxycarbonyl (**4d**) and 2-acetyl (**4e**) derivatives remain practically unchanged, whereas the corresponding steps of 2-cyano derivatives (**4a**—**c**) increase in height and eventually the current constant value *I* reaches that of the cations (**4d**) and (**4e**).

As far as the stability of 2-cyano radicals (**2a**—**e**) is concerned the reverse-pulse polarography and the cyclic voltammetry show that it decreases in the order (**2c**) ≫ (**2b**) > (**2a**). This different stability is clearly reflected in the PR voltammograms of 2-cyano-4-t-butyl-1-methylpyridinium cation (**4c**) and of 2-cyano-1-methylpyridinium cation (**4a**) shown in Figures 3 and 4, respectively. It should however be pointed out that both the RP voltammograms and the cyclic voltammetric curves show the presence of additional features (Figures 3 and 4) attributable to species (dimers, CN^-, *etc.*) deriving from the chemical evolution of the primary one-electron reduction products.

The presence of CN^- anions in solution is substantiated by voltammetric curves recorded with a glassy carbon electrode for a solution of (**4a**—**c**) electrolysed as perchlorate at the potential of the first polarographic step. In particular, one can observe an anodic step at *ca.* 1.1 V, which increases on addition of solid NaCN to the solution. The presence of cyanide anions at the electrode and their ability to react with the starting salts (Scheme 1) also explains the low current constant value *I* calculated for (**4a**—**c**) (*cf.* Table 1), as well as the increase observed on addition of protonating agents, which acting as traps for CN^- anions prevent their reaction with the starting cations.

Conclusions

The *N*-germylpyridinyl radicals studied in this work are fairly stable species which, analogous with those previously described,[8] are in equilibrium with the corresponding dimers.

As regards the *N*-methylpyridinyls (**2a**—**e**), the combined e.s.r. and electrochemical data indicate that their stability decreases in the order (**2f**) ≃ (**2e**) > (**2c**) ≫ (**2d**) > (**2b**) > (**2a**).

2-Cyano radicals (**2a**—**c**) appear to evolve with the loss of CN^- and in the case of (**2a**) the formation of 2,4-dicyano-1-methylpyridinyl (**2f**) has been substantiated by e.s.r. Further work is in progress to elucidate completely the anomalous electrochemical behaviour of the 2-cyano-*N*-methylpyridinium salts.

Experimental

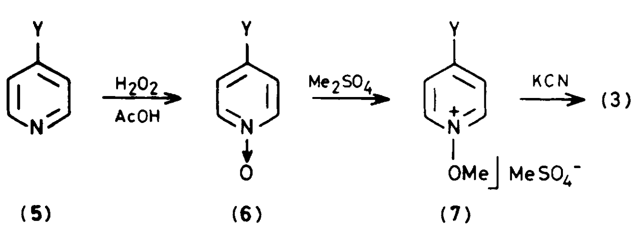
Compounds (**3a**, **d**, and **e**) were commercial products, whilst iodides (**4a**)[9] and (**4e**)[5] were prepared according to literature methods.

The free bases (**3b**, **c**, and **f**) were synthesized following the general procedure in Scheme 2, outlined by Feely and Beavers.[19]

Synthesis of (**7b**, **c**, *and* **f**).—Compound (**6b**) was obtained by carefully adding 36% H_2O_2 (0.48 mol) to 4-methylpyridine (0.32 mol in 70 ml of AcOH). The solution was stirred at 90 °C for 12 h. A second portion of H_2O_2 (0.26 mol) was added after 6 h. The cooled reaction mixture was diluted with water, neutralized with 20% NaOH solution, and extracted with CH_2Cl_2. The organic layer after evaporating to dryness gave (**6b**) in 65% yield: m.p. 184—185 °C (from benzene) (lit., 180—181 °C,[20] and 184—185 °C[21]). Compounds (**6c** and **f**) were prepared in a similar way; (**6c**) was obtained in 52% yield: m.p. 101—102 °C (from cyclohexane) (lit., 101—102 °C,[21] 104 °C[22]). Compound (**6f**) was isolated in 68% yield: m.p. 219—221 °C (from ethanol) (lit.,[21] 220—221 °C). Compound (**7b**) was obtained by heating equimolar amounts of (**6b**) and Me_2SO_4 (74 mol) at 90—100 °C for 3 h. After cooling, the residue was crystallized from acetone: m.p. 68—69 °C (lit.,[23] 69—73 °C). Compounds (**7c** and **f**) were isolated in a similar way as oils in 95 and 92% yield, respectively, and were used directly without further purification.

Synthesis of (**3b**, **c**, *and* **f**).—A cooled ethanolic solution of (**7b**) (26 mmol in 48 ml) was added dropwise under nitrogen to a stirred aqueous solution of KCN (78 mmol in 12 ml) keeping the temperature between −12 and −18 °C. Cooled water (120 ml) was then added to the mixture and after stirring for 3 h the mixture was extracted with CH_2Cl_2 (4 × 100 ml). The collected extracts were washed with water (3 × 50 ml). The organic layer was separated, dried (Na_2SO_4), and evaporated to dryness. Compound (**3b**) was obtained in 35% yield; m.p. 90—91 °C (lit.,[19] 89—91 °C). Compounds (**3c** and **f**) were prepared in a similar way. Compound (**3c**) was obtained in 45% yield: b.p. 106—108 °C at 0.25 mmHg (Found: C, 74.85; H, 7.65; N, 17.55. $C_{10}H_{12}N_2$ requires C, 74.96; H, 7.55; N, 17.49%).

Compound (**3f**) was obtained in 75% yield: m.p. 88—90 °C (lit.,[19] 89—91 °C).



Scheme 2.

Synthesis of (**4a**—**d**).—The free base (200 mmol in 30 ml of ethanol or acetone) and a two-fold excess of MeI were refluxed for 10—20 h. Pyridinium salts were isolated by cooling or solvent evaporation. 1,4-Dimethyl-2-cyanopyridinium iodide (**4b**): m.p. 175 °C (from acetone) (Found: C, 37.03; H, 3.38; N, 10.69. $C_8H_9IN_2$ requires C, 36.94; H, 3.49; N, 10.77%). 1-Methyl-2-cyano-4-t-butylpyridinium iodide (**4c**): m.p. 210 °C (from ethanol) (Found: C, 44.4; H, 5.1; N, 9.6. $C_{11}H_{15}IN_2$ requires C, 43.7; H, 5.0; N, 9.3%). 1-Methyl-2-ethoxycarbonylpyridinium iodide (**4d**): m.p. 97 °C (from ethanol) (Found: C, 36.85; H, 4.25; N, 4.8. $C_9H_{12}INO_2$ requires C, 36.9; H, 4.1; N, 4.8%). 2,4-Dicyanopyridine was converted directly into the corresponding 1-methanyl tosylate: m.p. 167 °C (from ethanol) (Found: C, 57.2; H, 4.1; N, 13.2. $C_{15}H_{13}N_3O_3S$ requires C, 57.1; H, 4.15; N, 13.3%).

Pyridinium perchlorates corresponding to (**4a** and **c**) were prepared by treating ethanolic solutions of (**4a** and **c**) with stoicheiometric quantities of $AgClO_4$ and purified by recrystallization (from ethanol): m.p.s 154 and 280 °C, respectively. The perchlorate of (**4d**) was a hygroscopic lyophilized material.

E.s.r. Measurements.—The *N*-germyl radicals (**1a**—**f**) have been generated by photolysis of t-butylbenzene solutions of the free bases (**3a**—**f**) containing small amounts of triphenylgermanium hydride and di-t-butylperoxide.[8b] A 1 KW high-pressure mercury lamp was used as the u.v. light source. The *N*-methylpyridinyls were generated by reduction of the salts (**4a**—**f**) with Bu^tOK in carefully deoxygenated DMSO solutions. The e.s.r. spectra were recorded on a Bruker ER 200 spectrometer equipped with an n.m.r. gaussmeter (calibration of the field) and standard variable-temperature accessories.

Electrochemical Measurements.—The electrochemical studies were carried out by direct current (d.c.) polarography, normal-pulse (NP) and reverse-pulse (RP) polarography, cyclic voltammetry (CV), and controlled-potential electroysis (CPE).

A multipolarograph (Amel 471) with a pulse time of 50 ms (sampling time 10 ms) was used for the polarographic techniques. A $Hg-Hg_2Cl_2$, $NaCl_{(sat.aq.)}$–DMF reference electrode[16] was used. Its potential was 56 mV *versus* a commercial aqueous saturated calomel electrode, the liquid junction potential being included. A dropping mercury electrode with a forced drop-time of 0.5—6.0 s was employed as a working electrode. A platinum wire was used as the auxiliary electrode. DMF (Merck, spectrophotometric grade) was purified as described previously.[16] Bu_4NClO_4, employed as supporting electrolyte, was vacuum dried at 60 °C for 2 d. Cyclic voltammograms were recorded (in the range 0.050—100 V s^{-1}) with an oscillographic polarograph (Amel 448) using the same cells as the polarographic measurements and a Beckmann dropping mercury electrode as a working electrode. The reversibility or otherwise of the d.c.,[24], RP,[17] and CV[18] voltammograms was established by conventional methods. The CP electrolyses for the coulometric determination of the number of electrons changed and radical generations were performed using a potentiostat (Amel 557/SU) coupled with an integrator (Amel 558) and a recorder

(Leeds and Northrup, Speedomax W). The electrolysis cell contained a magnetically stirred mercury pool (apparent area *ca.* 19 cm^2) as a working electrode and the same reference electrode as was employed in the polarographic measurements. The auxiliary electrode was a cylinder gauze of platinum placed inside a glass tube (diameter 19 cm) and was connected to the test solution *via* a methylcellulose–DMF–Bu_4NClO_4 plug or a sintered-glass disc. Argon (99.99% pure) was used to deoxygenate the solution under examination.

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