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Polyhalogenated Radical-anions

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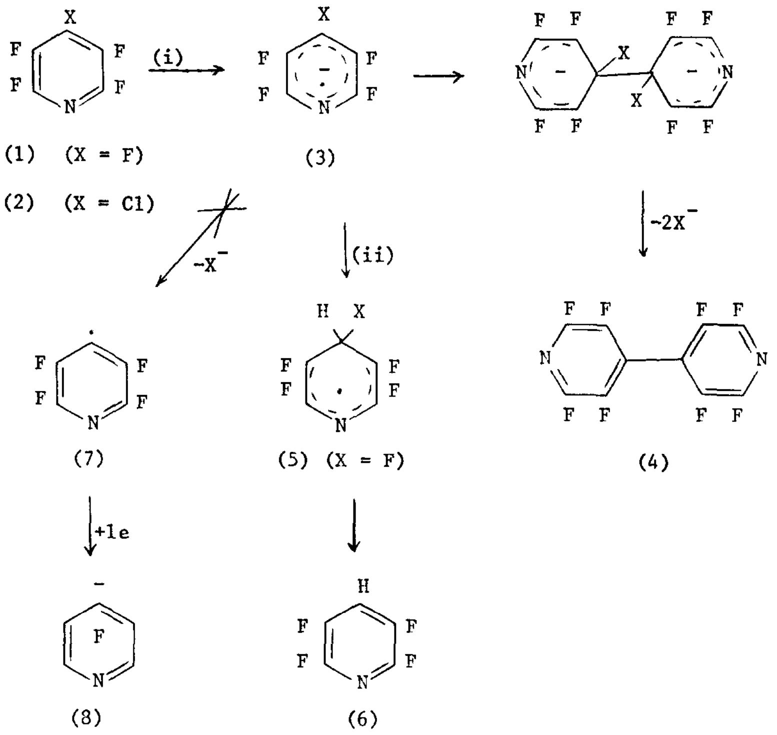
Summary. Electrochemical reduction of polyhalogenopyridines gives products from which structures of intermediate radical anions are inferred; the results agree with calculations.

Fully halogenated aromatic compounds provide interesting orientation problems in nucleophilic aromatic substitution, that are analogous to the well known orientation problems of electrophilic aromatic substitution.[1] Likewise, reactions of radical anions derived from fully halogenated aromatic compounds, provide a way to explore the electron distributions in these species, as inferred from structures of their reaction products.

We now find that polyhalogenated pyridines may be reduced at a mercury cathode and that, in each case, subsequent reaction occurs specifically at the 4-position. Pentafluoropyridine (1) gave perfluoro-4,4'-bipyridyl (4) while, in the presence of hydroquinone as a proton donor, 2,3,5,6-tetrafluoropyridine (6) was obtained. The most likely mechanism is that outlined in Scheme 1, involving coupling of the radical anion (3), followed by loss of halide ion, and this process is analogous to one described for the coupling of para-fluorobenzonitrile.[2] Hydroquinone efficiently intercepts the radical anion (3) and no bipyridyl derivative (4) is obtained. In principle, a mechanism involving nucleophilic attack by the radical anion (3) or the carbanion (8) on the polyhalopyridines (1) or (2) could be invoked but it is established that nucleophilic attack on (2) occurs specifically at the 2-position i.e. by displacement of fluorine in preference to chlorine.[3] Similarly, it is unlikely that (4) is produced via coupling of the radical (7) since (6) is obtained from pentafluoropyridine only in the presence of hydroquinone, whereas the radical (7) would be expected to abstract a hydrogen atom from solvent, electrolyte etc.

We have also reduced pentachloropyridine (9) at a lead cathode and a different situation obtains, to that obtained for the fluorinated pyridines. No significant amount of a bipyridyl derivative was detectable and tetrachloropyridine (13) was obtained, without the addition of a proton donor. The different course of the reactions of fluorinated and



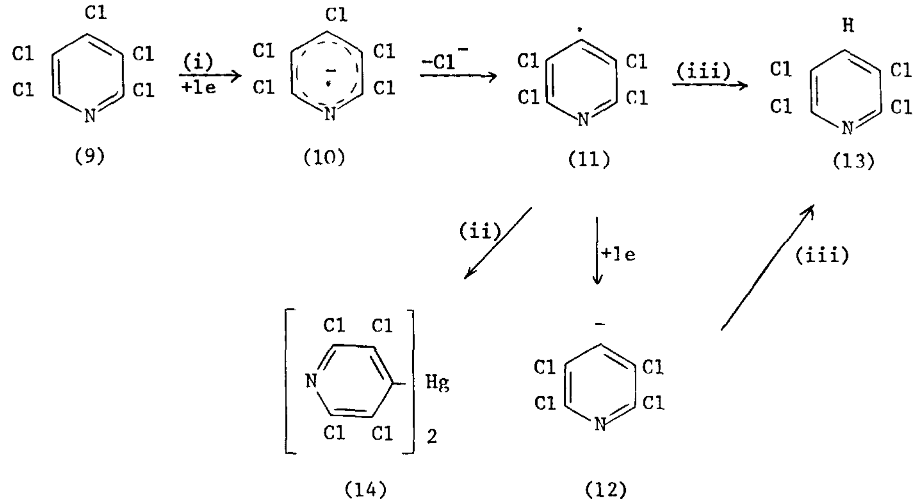
Scheme 1

(i) Hg cathode, D.M.F., Et_4NBF_4, -1.8V (S.C.E.).

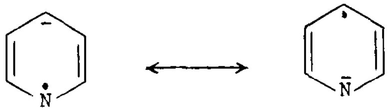
(ii) Hydroquinone.

chlorinated systems seems to stem from inhibition of the coupling of (10), due to the bulky *ortho*-chlorine atoms. Consistent with a process now involving (11), reduction of pentachloropyridine at a mercury cathode, gave bis(tetrachloropyridyl)mercury (14), in addition to (13).

It may be confidently inferred, therefore, that the radical anions derived from (1), (2), and (9) have a structure corresponding to (15a), (15b) and this agrees well with calculations. There are a variety of low lying states for radical anions derived from (1), (2) and (9) however the substitution pattern ensures that in each case there is a significant energetic preference for the $^2B_1$ states. These states may be envisaged as arising from the neutral molecules by population of the lowest unoccupied π molecular orbital of b_1 symmetry. Computations at the INDO level on perfluoropyridine support the contention that in simple valence bond parlance 15a and 15b contribute significantly to the overall wavefunction. Thus



(i) Pb cathode, D.M.F., Et_4NBF_4, -1.5V (S.C.E.); (ii) Hg cathode, -1.4V (S.C.E.); (iii) solvent/electrolyte.



(15a) (15b)

the π electron density and spin density distributions in the ground state $^2B_{1\pi}$ state predominantly place negative charge and spin density on nitrogen and C4 (cf. Table 1). A similar picture may be straightforwardly inferred for the radical anions derived from (2) and (9).

Table 1

Unpaired spin and charge distributions for the $^2B_{1\pi}$ state of pentafluoropyridine radical anion (π contributions ring atoms only)

	Unpaired spin density	Charge distribution
N	0.40	-0.46
C2(C6)	0.11	-0.09
C3(C5)	-0.04	-0.13
C4	0.42	-0.30

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