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POLYFLUOROPHENAZINES

A. G. Hudson, A. E. Pedler and J. C. Tatlow
Department of Chemistry, University of Birmingham,
Edgbaston, Birmingham 15.

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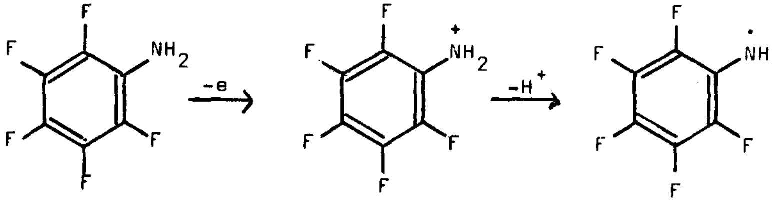
By electrochemical oxidation in acid solution aniline forms p-aminodiphenylamine, (1,2,3) p-aminophenol, (4) or emeraldine, (5) a poly(phenylenediamine), depending on the pH. N methylaniline, (6) NN dimethylaniline (7) and triphenylamine (8) in acid solution form the appropriate substituted benzidine by para coupling.

We have found that electrochemical oxidation of pentafluoroaniline gives octafluorophenazine and decafluoroazobenzene (9) in 6% and 18% yields respectively. The system used was an acetone: water: potassium acetate electrolyte and a platinum anode at a potential of 1.5v-1.6v (vs S.C.E.). The products were separated by fractional sublimation.

The initial reaction is thought to be the removal of an electron from the nitrogen of pentafluoroaniline to form the radical-ion (I), which by loss of a hydrogen ion affords the radical (II).

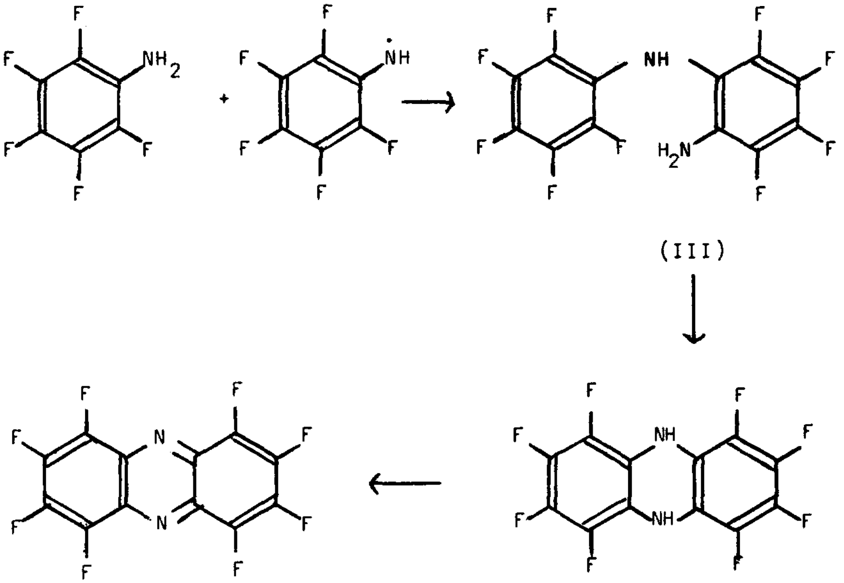


(I) (II)

Dimerization of (II) would then lead to decafluorohydrazobenzene (10) which subsequently oxidises to the observed decafluoroazobenzene.

Octafluorophenazine is thought to arise by attack of (II) at the ortho position of a pentafluoroaniline nucleus to form initially 2-aminononafluorodiphenylamine (III), which then undergoes further oxidation and an intramolecular cyclization to give 5,10-dihydro-octafluorophenazine (IV), which is readily oxidized to the observed octafluorophenazine (V).

An improved yield (40%) of octafluorophenazine was in fact obtained by the electrolysis of 2-aminononafluorodiphenylamine (11) (III).



(III)

(V) (IV)

The free radical displacement of fluorine from polyfluoroaromatic compounds has been proposed to account for the formation of tetrafluoroacridine by the pyrolysis of a pentafluoronitrosodiphenylketone (11) and pentafluorodiphenyl from benzoyl peroxide and hexafluorobenzene (12).

Octafluorophenazine is a yellow crystalline solid (m.p. 234°) which was identified by elemental analysis, high resolution mass spectrometry and N.M.R. spectrometry, the ^{19}F spectrum showing two signals in the ratio 1:1, with chemical shifts of 144.6ϕ* and 149.8ϕ*. Further characterization was by the formation of 5,10-dihydro-octafluorophenazine (m.p. 186°) by catalytic hydrogenation.

Electrolysis of fluoroanilines and aminofluorodiphenylamines has been used to prepare other fluorophenazines. Thus, by electrochemical oxidation, p-methoxytetrafluoroaniline (13) gave 2,7-dimethoxyhexafluorophenazine (m.p. 218.5-219.5°), 2-amino-5-methoxyoctafluorodiphenylamine gave 2-methoxyheptafluorophenazine (m.p. 131-132°) and 2-amino-2^{1},3,3^{1},4,5,5^{1},6,6^{1}-octafluorodiphenylamine gave 1,3,4,6,7,8,9-heptafluorophenazine (m.p.187.5-188.5°). 1,2,3,4-tetrafluorophenazine (m.p. 226-227°) was prepared in 33% yield by the electrochemical oxidation of 2-amino-2^{1},3,4,5,6-pentafluorodiphenylamine. The tetrafluorophenazene was characterized by N.M.R. spectroscopy, mass spectrometry, elemental analysis, and the formation of 5,10-dihydro-1,2,3,4-tetrafluorophenazine (m.p. 150-152°) by catalytic hydrogenation.

For the electrochemical cyclisation of an aminofluorodiphenylamine to occur, the presence, in the ring not containing the -NH_2 group, of a fluorine ortho to the NH would appear to be essential. Thus, electrolysis of 2-amino-3,4,5,6-tetrafluorodiphenylamine gave only 1,2,3,4-tetrafluorophenazine in very poor yield.

Further work is in progress concerning the chemistry of these polyfluorophenazines.

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