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THE ELECTROCHEMICAL OXIDATION OF POLYFLUOROAROMATIC AMINES—I

THE SYNTHESIS OF FLUOROPHENAZINES

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Abstract—Octafluorophenazine and decafluoroazobenzene have been obtained by the electrochemical oxidation of pentafluoroaniline at a platinum anode. Similarly, octafluorophenazine 2*H*-heptafluorophenazine and 1,2,3,4-tetrafluorophenazine have been obtained from 2-aminononafluorodiphenylamine, 2-amino-4′*H*-octafluorodiphenylamine and 2-amino-2′,3,4,5,6-pentafluorodiphenylamine, respectively. The synthesis of 2-nitro-, and 2-amino-polyfluorodiphenylamines is also described.

IN a previous preliminary communication[1] we briefly reported some results on the electrochemical oxidation of polyfluoroaromatic amines. We now give them in detail and describe the synthesis of a number of 2-nitro- and 2-aminopolyfluorodiphenyl amines. By the electrochemical oxidation of pentafluoroaniline at a platinum anode at a potential of +1·5 –+1·6 V (VS S.C.E.), using an acetone: water: potassium acetate electrolyte, decafluoroazobenzene[2] (identified by m.p. and IR spectrum) and octafluorophenazine were obtained in 18% and 6% yields respectively. Octafluorophenazine was identified by accurate mass measurement and chemical analysis (correct for $C_{12}F_8N_2$). The ^{19}F NMR spectrum (in T.F.A.) showed only two signals in the ratio 1:1, correct for octafluorophenazine, while the UV and IR spectra were consistent with the proposed structure. The identification was confirmed by reduction of the phenazine to 5,10-dihydrooctafluorophenazine, which was readily oxidized back to the parent compound. Octafluorophenazine was also obtained, and in better yield (40%), by the electrochemical oxidation of 2-aminononafluorodiphenylamine[3], although the attempted chemical cyclization of the amine using sodium hydride and n-butyl lithium was unsuccessful.

Other polyfluorophenazines have also been synthesized electrochemically from suitable amino-polyfluorodiphenylamines. Thus, 2*H*-heptafluorophenazine was obtained from 2-amino-4′*H*-octafluorodiphenylamine and 1,2,3,4-tetrafluorophenazine from 2-amino-2′,3,4,5,6-pentafluorodiphenylamine. The tetrafluorophenazine was also obtained from 2-nitro-3,4,5,6-tetrafluorodiphenylamine by treatment with iron filings at 280–300°. The structures of the phenazines were confirmed by their NMR, IR and UV spectra and 1,2,3,4-tetrafluorophenazine was reduced to 5,10-dihydrotetrafluorophenazine. The electrolytic oxidation of 2-amino-3,4,5,6-tetrafluorodiphenylamine and 2-amino-2′-fluorodiphenylamine was also investigated. Only a small yield of tetrafluorophenazine was obtained from the former, while no phenazine was obtained from the latter. However, subsequent experiments showed that phenazine itself was oxidized at a lower potential than that used for the oxidation of the amine.

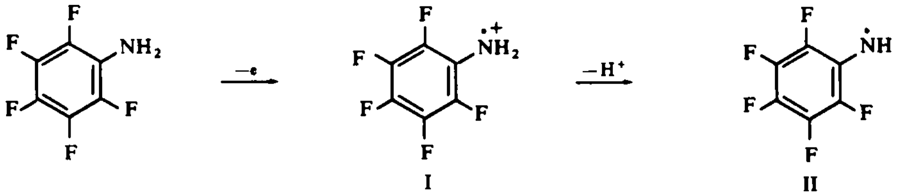
The m.ps of both octafluoro- and 1,2,3,4-tetrafluoro-phenazine were found to be anomalous. The first samples prepared[1] were found to melt at 233–235° and 226–227° respectively (cited[4] by others 238·5–239·5 and 233–234°). From preparations done later, however, the products melted at 259–260° and 262–263° respectively, and we were then unable to obtain the lower melting form again.

The amino-polyfluorodiphenylamines used were prepared by the reduction of the corresponding nitro-polyfluorodiphenylamines using a Pd/C catalyst. The nitro-polyfluorodiphenylamine compounds were generally synthesized by treating the lithium salt of the appropriate aromatic amine with a polyfluoronitrobenzene. This reaction differs from most nucleophilic displacement reactions[5] of polyfluoroaromatic compounds in that unusually high proportions of *ortho* isomer are obtained. However, some other reactions[6] involving pentafluoronitrobenzene also give high proportions of ortho product. The lithium salt of pentafluoroaniline reacted with pentafluoronitrobenzene to give 2-nitrononafluorodiphenylamine (m.p. 79°)[3], which was reduced to form 2-aminononafluorodiphenylamine (m.p. 45°)[3]. For the preparation of 2-nitro-4^1H-octafluorodiphenylamine it was necessary to react 2,3,5,6-tetrafluoroaniline with pentafluoronitrobenzene. Owing to the possibility of attack by n-butyl lithium on the 4*H*-position as well as on $—NH_2$, sodium hydride was used to form the amine salt: a good yield of the 2-nitro-polyfluorodiphenylamine was nevertheless obtained. 2-Amino-3,4,5,6-tetrafluorodiphenylamine was prepared by an alternative route. Although the 2-nitro-3,4,5,6-tetrafluorodiphenylamine precursor may be obtained by the reaction of the lithium anilide on pentafluoronitrobenzene, our sample was made by heating the 1:1 complex formed between aniline and pentafluoronitrobenzene.[3] The nitro-compound was then reduced to the amine in the usual way. The structures of the 2-nitro- and 2-amino-polyfluorodiphenylamine compounds were confirmed by chemical analysis, UV, IR, and NMR spectroscopy, which were in agreement with the assigned structures.

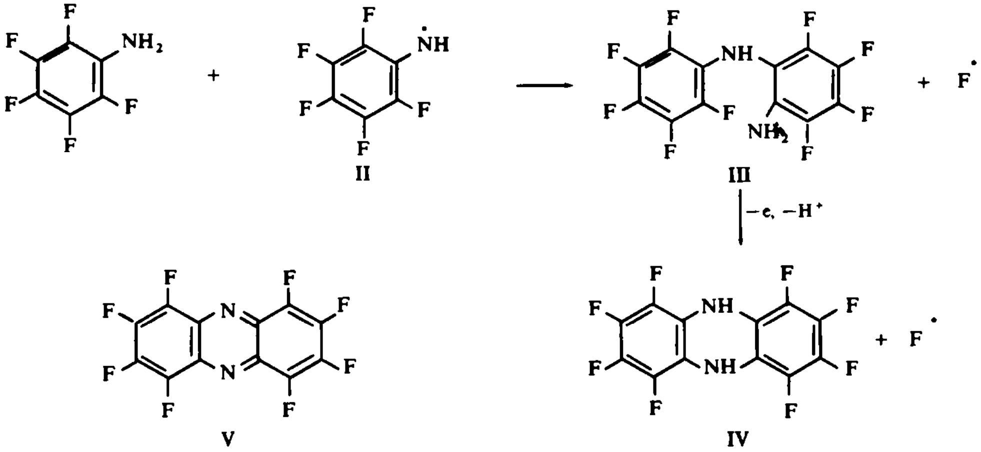
The electrochemical oxidation of aniline and n-alkyl and aryl substituted aniline derivatives has been extensively studied. In acid solution aniline gives rise to *p*-amino diphenylamine,[7] *p*-amino phenol[8] or emeraldine[9] (a polyphenylene diamine), depending on pH. In alkaline solutions, primary aromatic amines yield the corresponding azobenzene.[10] Electrochemical oxidation of N-methylaniline,[11] N,N-dimethylaniline[12] and triphenylamine,[13] in both acid and mildly alkaline solutions form the appropriate substituted benzidene by *para* coupling.

Two mechaisms have been proposed to account for the products. The first[7] involves the formation of the $C_6H_5NH^•$ radical by loss of an electron and hydrogen ion from aniline, which then, by appropriate dimerization reactions, gives rise to *p*-aminophenol and *p*-aminodiphenylamine. Further oxidation of the latter compound leads to emeraldine. A more recent mechanism,[9] applicable to the reactions of both aniline and N-aryl and-alkyl substituted aniline, involves $C_6H_5NH_2^{•+}$ and $C_6H_5NR_2^{•+}$ radical ions, which dimerize with the loss of two hydrogen ions to give the appropriate products.

We believe the results we have obtained to be more consistent with the participation of $C_6F_5NH^•$ radicals in the reaction mechaism. Thus the initial reaction is thought to be loss of an electron from pentafluoroaniline to form the radical-ion I, which by loss of a hydrogen ion affords the radical II. Dimerization of II would then lead to decafluorohydrazobenzene, which subsequently oxidizes 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-amino-nonafluorodiphenylamine [III], which undergoes further oxidation, followed by intramolecular cyclization to give 5,10-dihydrooctafluorophenazine [IV]. This is then further oxidized to octafluorophenazine [V]. An improved yield of V was, in fact,



obtained by the electrolysis of a solution of III. The free radical displacement of fluorine from polyfluoroaromatic compounds has been previously proposed to account for the formation of tetrafluoroacridine by the pyrolysis of pentafluoronitrosodiphenylketone[14] and of 2,3,4,5,6-pentafluorodiphenyl from benzoyl peroxide and hexafluorobenzene.[15] For the electrochemical cyclization of an amino-polyfluorodiphenylamine to occur, the presence, in the ring not containing the—NH_2 group, of a fluorine atom *ortho* to the—NH group could appear to be essential. Thus, electrolysis of 2-amino-3,4,5,6-tetrafluorodiphenylamine gave 1,2,3,4-tetrafluorophenazine in only very poor yield, although 2-amino 2′,3,4,5,6-pentafluorodiphenylamine gave an improved yield of the tetrafluorophenazine.

The formation of decafluoroazobenzene by dimerization of the $C_6F_5NH_2^{\cdot+}$ radical ion is difficult to envisage. In addition, the stability of the polyfluoro radical-ion (I) must be significantly less than that of the hydrocarbon analogue, particularly in the alkaline medium used, where it is likely to lose a hydrogen ion rapidly to yield the radical, II. Although it is possible to draw up a reaction scheme for the oxidation of an amino-polyfluorodiphenylamine to a polyfluorophenazine involving the $C_6F_5NH_2^{\cdot+}$ species, it is difficult to extend the argument to account for the products of the oxidation of pentafluoroaniline. The two reaction mechanisms require a different coulommetry for the oxidation of both pentafluoroaniline and 2-amino-polyfluorodiphenylamine. Thus if $C_6F_5NH^{\bullet}$ radicals participate the oxidation should require 3 electron/mole, while a $C_6F_5NH_2^{\cdot +}$ radical-ion mechanism requires only 2-electron/mole are required although complications arise since it is likely that both decafluorohydrazobenzene[2] and 5,10-dihydropolyfluorophenazine will be susceptible to oxidation by atmospheric oxygen, thus possibly reducing the number of coulombs required for the reduction process.

EXPERIMENTAL

The apparatus for electrochemical oxidations consisted of a 700 ml flask as anode compartment, connected *via* a glass tube (5 cm × 2·5 cm d.) to a cathode compartment (14·5 cm × 3·5 cm d.) The contents of the two compartments were prevented from mixing by a sintered glass disc sealed into the connecting tube. The anode was of platinum (10 cm × 5 cm) and the cathode a carbon rod. Oxidations were carried out in a mixture of acetone (200 ml), water (350 ml) and KOAc (100 g) at a fixed anode potential (measured against a S.C.E.), by adjusting the voltage applied across the cell electrodes. The current passing at the beginning was usually ca. 500 m.a., falling to ca. 50 m.a., when the electrolysis was stopped. The total number of coulombs passed during the electrolysis was calculated from the current/-time curve.

At the end, the anolyte was distilled under reduced press to remove acetone and filtered. The solid residue was dried over P_2O_5 and fractionally sublimed under reduced press. Known compounds were identified by a comparison of IR spectra. NMR spectra were recorded on samples dissolved in trifluoroacetic acid unless otherwise stated. All data quoted on the *delta* scale with high field (low frequency) shifts negative. The reference standards ($\delta = 0·0$) are TMS and CCl_3F for ^1H and ^{19}F spectra respectively.

Electrolysis of pentafluoroaniline. Pentafluoroaniline (10 g) was electrolysed in the standard electrolyte (500 ml) at a potential of +1·5–+1·6 V. After passing 10,560 coulombs, when the current had fallen to 70 m.a., the electrolysis was stopped and the solid product (10·9 g) obtained as described. Fractional sublimation gave (i) decafluoroazobenzene (1·78 g) and (ii) a yellow solid which was recrystallized from CCl_4 and identified as *octafluorophenazine* (0·55 g), m.p. 259–260°. (Found: C, 44·1; H, 0·0. $C_{12}F_8N_2$ requires: C, 44·4; H, 0·0%). The molr wt by high resolution mass spectrometry was 323·991 ($C_{12}F_8N_2$ requires: 323·993). The UV spectrum (in ethanol) showed absorptions at 258 and 368 nm. with $\varepsilon = 9·1 \times 10^4$ and $5·9 \times 10^3$ respectively and the ^{19}F NMR spectrum showed two signals in the ratio 1:1, with chemical shifts δ −144·6 and −149·8 consistent with the proposed structure. When first prepared this compound had m.p. 233–235° but subsequently all samples isolated have had m.p. 259–260°.

Reduction of octafluorophenazine. Octafluorophenazine (0·66 g) was dissolved in dry ether (150 ml) and Pd/C (0·1 g, 10% Pd) added. The suspension was hydrogenated, and the mixture dried ($MgSO_4$), filtered, and evaporated to give a product (0·65 g), which was crystallized (CCl_4) to give 5,10-*dihydro-octafluorophenazine*, (0·21 g) m.p. 185–187° (Found: C, 43·9; H, 0·9; N, 8·3. $C_{12}H_2F_8N_2$ requires: C, 44·2; H, 0·6; N, 8·3%). Mass spectrometry gave a top mass peak of 326 (required 326) and the IR spectrum showed an absorption maximum at 3440 cm^{-1} typical of >NH. On shaking with Br_2/CCl_4 octafluorophenazine was recovered (yield ~90%).

Electrochemical oxidation of 2-amino-nonafluorodiphenylamine. The amine (2·0 g) was electrolysed in the standard electrolyte (500 ml) at a potential of +1·4–+1·5 V and 1660 coulombs passed. After removal of the acetone, a product (1·51 g) was obtained as described above, which was sublimed to give octafluorophenazine (0·77 g) only.

Electrolysis of 2-amino-4' H-*octafluorodiphenylamine.* The diphenylamine (2·9 g) was electrolysed using the standard electrolyte (500 ml) at an anode potential of +1·5–+1·6 V, and 2360 coulombs passed. The anolyte was treated in the usual way to give a solid (2·15 g) which was sublimed to give a yellow product (0·66 g). Recrystallization from light petroleum (b.p. 40–60°) gave 2-H-*heptafluorophenazine* (0·55 g) m.p. 189–191° (Found: C, 47·0; H, 0·7; N, 9·1. $C_{12}HF_7N_2$ requires: C, 47·1; H, 0·3; N, 9·2%). The ^1H NMR spectrum consisted of a broad singlet, chemical shift δ 7·82, and the ^{19}F spectrum of six signals in the ratio 1:1:1:1:2:1 at δ −123·0, −124·9, −145·2, −147·0, −151·2 and −154·1 respectively.

Electrolysis of 2-*amino*-2',3,4,5,6-*pentafluorodiphenylamine.* The amine (0·94 g) was electrolysed in the standard electrolyte (500 ml) at an anode potential of +1·5–+1·6 V, and 330 coulombs passed. The anolyte was treated as described above to give a product (1·14 g), which was sublimed to give (i) starting material (0·09 g), identified by a comparison of IR spectra and (ii) 1,2,3,4-*tetrafluorophenazine* (0·29 g), m.p. 262–263° (recrystallized from EtOH). (Found: C, 56·8; H, 1·8; $C_{12}H_4F_4N_2$ requires: C, 57·1; H, 1·6%). The UV spectrum (EtOH) showed absorptions at 252 and 362 nm, ε 1·19 × 10^5 and 0·96 × 10^4 respectively. The ^1H NMR spectrum showed one signal at 7·0 ppm low field from C_6H_{12} and the ^{19}F NMR spectrum showed two signals in the ratio 1:1, chemical shifts δ −141·95 and −149·0, in agreement with the proposed structure. The original preparations had m.p. 226–227° but subsequently all samples isolated had m.p. 262–263°.

Reduction of 1,2,3,4-*tetrafluorophenazine*. The phenazine (0·2 g) was dissolved in ether (50 ml) and Pd/C (0·1 g, 10% Pd) added. The mixture was hydrogenated, filtered under N_2, and evaporated to give a solid (0·2 g), which was recrystallized (CCl_4) to give blue crystals of 5,10-*dihydro*-1,2,3,4-*tetrafluorophenazine* (0·09 g) m.p. 150–152° (with dec) (Found: C, 56·5; H, 2·5; N, 10·7. $C_{12}H_6F_4N_2$ requires: C, 56·7; H, 2·4; N, 11·0%). Mass spectrometry gave a top mass peak of 254 (required: 254). The IR spectrum showed an absorption maximum at 3440 cm^{-1} (>NH).

Electrolytic oxidation of 2-*amino*-3,4,5,6-*tetrafluorodiphenylamine*. The amine (0·85 g) was electrolysed using the usual electrolyte (500 ml) at +1·4–+1·5 V, and 480 coulombs passed. The solution was treated as described above to give a residue (1·02 g) which was sublimed to give 1,2,3,4-tetrafluorophenazine (0·012 g).

Electrolytic oxidation of 2-*amino*-2′-*fluorodiphenylamine*. The diphenylamine (1·5 g) was oxidized in the usual way at +1·0–+1·1 V and 1930 coulombs passed. The solid (1·7 g) remaining after removal of the acetone was sublimed. No phenazine was obtained: other experiments showed that phenazine itself was susceptible to electrochemical oxidation at +1·0–+1·5 V in the medium employed.

2-*Nitro*-4′H-*octafluorodiphenylamine*. 2,3,5,6-Tetrafluoroaniline (5·0 g) in dry ether (300 ml) was stirred under N_2 with sodium hydride (1·47 g, 50% w/w mineral oil dispersion) for 2 hr. The suspension was gently warmed until H_2 evolution ceased, and the mixture added slowly to a soln of pentafluoronitrobenzene (6·45 g) in dry ether (200 ml). The resulting red ethereal suspension was refluxed for 24 hr and then allowed to cool. The ethereal soln was decanted from unreacted sodium hydride, washed with 4N HCl (3 × 50 ml), dried ($MgSO_4$) and evaporated to give a solid residue (9·95 g). This was separated on an alumina column (eluant, light petroleum b.p. 40–60°: benzene = 2:1) to give 2-*nitro*-4′H-*octafluorodiphenylamine* (3·9 g), m.p. 79·5–80·5°. (Found: C, 40·3; H, 1·0; N, 8·1. $C_{12}H_2F_8N_2O_2$ requires: C, 40·2; H, 0·6; N, 7·8%). The IR spectrum showed an absorption maximum at 3370 cm^{-1} (>NH) and 3080 cm^{-1} (aromatic C—H). The ^1H NMR spectrum (in CCl_4) showed two signals in the ratio 1:1 with chemical shifts δ 7·28 (>NH) and δ 6·85 (aryl H). The latter signal was a triplet of triplets (J = 9·75 Hz and 7·1 Hz). The ^{19}F NMR spectrum (in CCl_4) showed six signals in the ratio 2:1:1:1:2:1: with chemical shifts δ −139·2, −144·9, −147·4, −149·9, −153·1, and −162·3 respectively. The NMR spectra are thus consistent with the proposed structure.

2-*Amino*-4′H-*octafluorodiphenylamine*. 2-Nitro-4′*H*-octafluorodiphenylamine (4·5 g) was dissolved in EtOH (100 ml) and Pd/C (0·1 g, 10% Pd) added. The suspension was hydrogenated, filtered under N_2, and the EtOH evaporated to give a solid residue (3·8 g), which was sublimed to give 2-*amino*-4′H-*octafluorodiphenylamine* (2·70 g) m.p. 83–85°. (Found: C, 44·1; H, 1·5; N, 8·8. $C_{12}H_4F_8N_2$ requires: C, 43·9; H, 1·2; N, 8·5%). The IR spectrum showed absorptions at 3440, 3360 and 3240 cm.$^{-1}$ (>NH and $-NH_2$), and at 3090 (aromatic C—H). The ^1H NMR spectrum (in CCl_4) showed three signals in the ratio 1:2:1 with chemical shifts δ 5·07 (>NH), 4·01 ($-NH_2$) and 6·62 (aryl H) respectively. The latter was a multiline signal with J = 10 Hz and 7·2 Hz. The ^{19}F NMR spectrum (in CCl_4) showed five signals in the ratio 2:1:3:1:1 with chemical shifts δ −140·0, −150·0, −159·3, −162·6 and −173·3 respectively, consistent with the proposed structure.

2-*Nitro*-2^1,3,4,5,6-*pentafluorodiphenylamine*. n-BuLi (10 ml, 0·14 g/ml) was added, over a period of 10 min, to a stirred solution of *o*-fluoroaniline (2·6 g) in dry ether (200 ml) under N_2, and the stirring continued for a further 15 min. The mixture was added slowly (20 min) to a solution of pentafluoronitrobenzene (5·0 g) in dry ether (200 ml). After the addition the mixture was refluxed for 5 min, washed with 4N H_2SO_4, dried ($MgSO_4$) and evaporated to leave a product (5·8 g). This was purified by column chromatography (alumina, light petroleum 40–60° solvent) to give orange crystals of 2-*nitro*-2^1,3,4,5,6-*pentafluorodiphenylamine* (2·77 g), m.p. 78–80·5°. (Found: C, 47·7; H, 1·9; N, 9·2. $C_{12}H_5F_5N_2O_2$ requires: C, 47·4; H, 1·7; N, 9·2%). The IR spectrum showed an absorption band at 3370 cm^{-1} (>NH). The ^1H NMR spectrum (in deuteroacetone) consisted of two signals in the ratio 1:4, chemical shifts δ 8·4 (>NH) and 7·4 to 8·0 (aryl H) respectively. The latter signal was a multiplet. The ^{19}F NMR spectrum (in deuteroacetone) showed five signals in the ratio 1:1:1:1:1, chemical shifts δ −129·7, −147·1, −151·5, −166·0 and −148·8, consistent with the proposed structure.

2-*Amino*-2^1,3,4,5,6-*pentafluorodiphenylamine*. 2-Nitro-2^1,3,4,5,6-pentafluorodiphenylamine (1·91 g) was dissolved in ethanol (100 ml) and Pd/C (0·1 g, 10% Pd) added. The suspension was hydrogenated, filtered, and the ethanol evaporated to give a white solid (1·71 g). Recrystallization from light petroleum (b.p. 40–60°) gave 2-*amino*-2^1,3,4,5,6-*pentafluorodiphenylamine* (1·23 g) m.p. 76–78°. (Found: C, 52·3; H, 2·8; $C_{12}H_7F_5N_2$ requires: C, 52·6; H, 2·6%). The IR spectrum showed absorption maxima at 3490, 3440 and 3390 cm^{-1} typical of >NH and $-NH_2$.

2-*Nitro*-3,4,5,6-*tetrafluorodiphenylamine*. To pentafluoronitrobenzene (4·42 g) in dry ether (150 ml) was added aniline (1·93 g), and the ether evaporated to yield a yellow solid (6·1 g), m.p. 65–68° the 1:1 complex between pentafluoronitrobenzene and aniline.[3] The solid (3·7 g) was heated (85°) in a sealed tube (2 hr), when the contents were dissolved in ether, dried ($MgSO_4$) and evaporated to yield an orange product, which was sublimed to give 2-nitro-3,4,5,6-tetrafluorodiphenylamine (1·32 g) m.p. 106°, with an IR spectrum identical with that of an authentic sample.[3]

2-*Amino*-3,4,5,6-*tetrafluorodiphenylamine*. 2-Nitro-3,4,5,6-tetrafluorodiphenylamine (1·1 g) was dissolved in EtOH (50 ml) and Pd/C catalyst (0·1 g, 10% Pd) added and the mixture hydrogenated. The soln was filtered under N_2 and the ethanol evaporated to give 2-amino-3,4,5,6-tetrafluorodiphenylamine, (0·85 g) m.p. 101°, with an IR spectrum identical with that of an authentic sample.[3]

2-*Fluoro*-2′-*nitrodiphenylamine*. n-BuLi (18·5 ml, 0·14 g/ml) in dry ether (20 ml) was added slowly (10 min) to a stirred soln of o-fluoroaniline (4·72 g) in dry ether (200 ml). The soln was stirred for 15 min under N_2. The mixture was then added over a period of 15 min to a solution of *o*-fluoronitrobenzene (6·0 g) in dry ether (200 ml) with stirring. The resulting red soln was refluxed for 27 hr, washed with 4N HC*l* (3 × 50 ml), dried ($MgSO_4$) and evaporated. The residue (7·7 g) was separated on an alumina column (light petroleum b.p. 40–60°) to give a product (7·59 g) which, after recrystallization twice (light petroleum b.p. 40–60°) gave 2-*fluoro*-2′-*nitrodiphenylamine* (3·36 g) m.p. 73·5–74·5°. (Found: C, 62·0; H, 4·2; N, 12·2. $C_{12}H_7F_2N_2O_2$ requires: C, 62·1; H, 3·9; N, 12·1%). The IR spectrum showed an absorption maximum at 3350 cm^{-1} (>NH).

2-*Amino*-2′-*fluorodiphenylamine*. 2-Fluoro-2′-nitrodiphenylamine (2·3 g) was dissolved in EtOH (100 ml) and Pd/C (0·1 g, 10% Pd) added, and the mixture hydrogenated. The suspension was filtered under N_2, and the EtOH evaporated to give a product (2·1 g), which was recrystallized from light petroleum (b.p. 40–60°) to give 2-*amino*-2′-*fluorodiphenylamine* (1·5 g) m.p. 72–73°. (Found: C, 71·5; H, 5·4; N, 13·6. $C_{12}H_{11}FN_2$ requires: C, 71·3; H, 5·5; N, 13·9%). The IR spectrum showed absorptions at 3220 and 3320–3440 cm^{-1} typical of >NH and $-NH_2$.

Attempted chemical cyclization of 2-amino-nonafluorodiphenylamine

(*a*) *Sodium hydride in ether*. The diphenylamine (0·73 g) in ether (120 ml) was added slowly (40 min) to sodium hydride (0·40 g, 50% w/w mineral oil) in dry ether (50 ml) and the mixture refluxed for 20 hr. The mixture was washed with 4N HC*l* (3 × 50 ml), dried ($MgSO_4$) and evaporated to give a product (0·89 g) from which octafluorophenazine was not obtained by sublimation.

(*b*) *Sodium hydride in dioxan*. The diphenylamine (1·0 g) in dry redistilled dioxan (50 ml) was refluxed for 60 min with sodium hydride (0·28 g, 50% w/w mineral oil), and the resulting mixture poured into water (400 ml). The aqueous solution was ether extracted (3 × 100 ml), and the ethereal extracts washed with H_2O (4 × 100 ml) dried ($MgSO_4$) and evaporated to give a product (1·12 g). The product was sublimed to give 2-amino-nonafluorodiphenylamine (0·4 g) only.

(*c*) *n-Butyl lithium in ether*. n-BuLi (1 ml, 0·15 g/ml) in dry ether (15 ml) was added (5 min) to the amine (0·4 g) in dry ether (15 ml), and the mixture stirred for 60 min, and then refluxed for a further 12 hr. The ether solution was washed with 4N HC*l*, dried ($MgSO_4$) and evaporated to give a solid (0·37 g). No octafluorophenazine could be isolated from this.

Chemical cyclization of 2-*nitro*-3,4,5,6-*tetrafluorodiphenylamine*. The diphenylamine, prepared by heating to 85° the 1:1 complex formed between pentafluoronitrobenzene and aniline[3] was heated for 60 min at 280–300° with degreased iron filings. The mixture was then powdered and Soxhelet extracted with acetone for 12 hr. The soln was evaporated to a residue (1·12 g), which was sublimed to give 1,2,3,4-tetrafluorophenazine (0·74 g), m.p. 226–227°, identical with the product obtained by electrochemical oxidation of 2-amino-2′,3,4,5,6-pentafluorodiphenylamine.

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