Cyclizations. Part 1. Electrochemical and Photochemical Reactions of 1-(4-Fluorophenyl)-5-(2-halogenophenyl)tetrazoles

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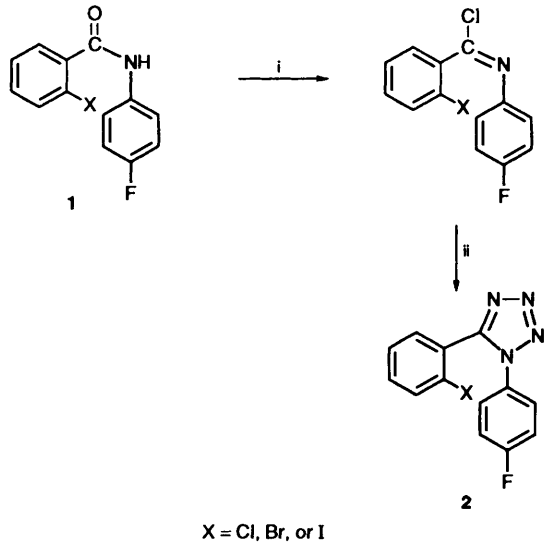
Electrochemical reduction of the title compounds, where the halogen substituent is Cl, Br or I, leads to cleavage of the carbon–halogen bond to leave a phenyl radical. Competition then follows between intramolecular radical substitution giving 7-fluorotetrazolo[1,5-*f*]phenanthridine and further reduction of the radical, then protonation, giving 1-(4-fluorophenyl)-5-phenyltetrazole. Substitution predominates but reduction and protonation becomes a more competing reaction when the halogen is Br or I. Photochemical reaction of the title compounds shows competition between carbon–halogen bond cleavage to give 7-fluorotetrazolo[1,5-*f*]phenanthridine and loss of nitrogen followed by cyclization to give 2-halogenophenyl-5-fluorobenzimidazole. Carbon–halogen bond cleavage predominates and becomes the only reaction when the halogen is I. The fluorine substituent allows the determination of product yields by ^{19}F NMR spectroscopy.

Electrochemical reduction,[1] reactions with solvated electrons in liquid ammonia[2,3] and also photolysis[4] of the carbon–halogen bond, when applied to in halogenoarenes, are all potential sources of aryl radicals. Aryl radicals so formed can undergo rapid intramolecular substitution onto an adjacent benzene ring thus leading to the formation of a new six-membered ring. Examples of the electrochemically initiated ring-closure process have been given.[5–7] A related and photochemically initiated ring closure may involve aryl radicals formed by bond homolysis, but another recognised mechanism involves an initial electrocyclic ring closure, followed by loss of hydrogen halide.[4] It is of interest to compare the electrochemical and photochemical reactions of 1-(4-fluorophenyl)-5-(2-halogenophenyl)tetrazoles **2**, particularly because in the photochemical reaction there is a possible competition from photoelimination of nitrogen from the tetrazole ring.[8]

A fluorine substituent was placed on one benzene ring so as to aid quantitative analysis of the reaction mixtures by ^{19}F NMR spectroscopy and the wide range of fluorine chemical shifts is an advantage. The tetrazoles **2** were prepared from the corresponding benzamides **1** by conversion into the imino chloride and then reaction with sodium azide. Previous work had indicated that the latter reaction proceeds best in anhydrous dimethylformamide and with rigorous exclusion of moisture.[7]



X = Cl, Br, or I

Reagents: i, PCl_5; ii, NaN_3 in $HCONMe_2$

Electrochemical Reduction.—Electrochemical reduction of aryl halides in aprotic solvents involves the addition of one electron to the lowest energy unoccupied π-orbital to form a radical-anion [eqn. (1)]. This intermediate decomposes to generate a σ-radical and a halide ion [eqn. (2)].

$$Ar\text{-}X + e \rightleftharpoons Ar\text{-}X^{\neg\bullet -} \quad (1)$$

$$Ar\text{-}X^{\neg\bullet -} \longrightarrow Ar^{\bullet} + X^{-} \quad (2)$$

The rate of the carbon–halogen bond cleavage depends on the energy level of the lowest π*-orbital and on the carbon–halogen bond strength.[9,10]

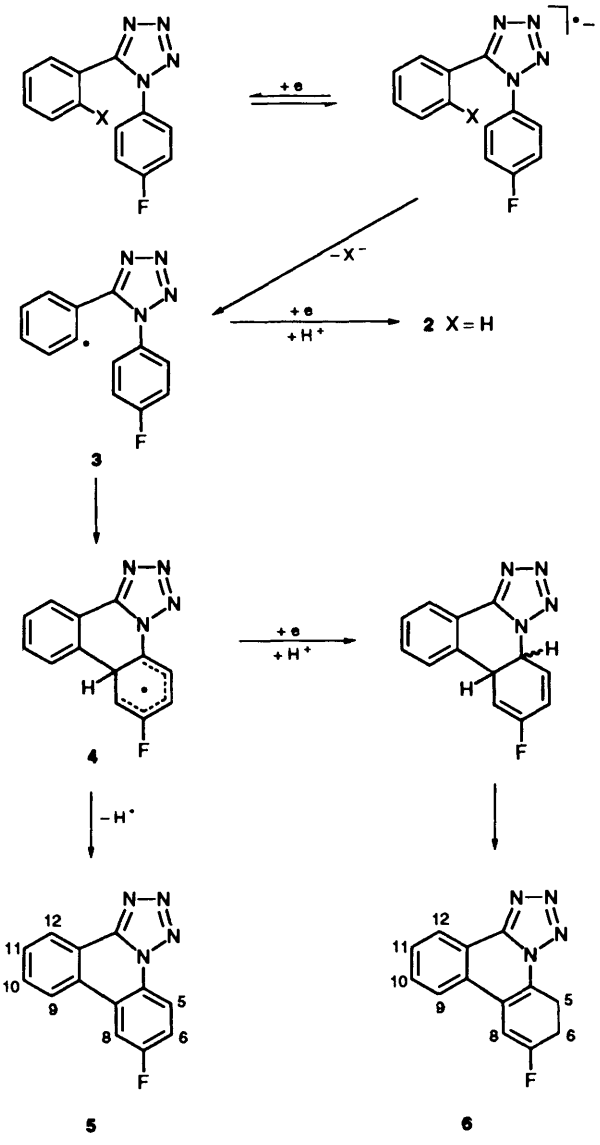
The carbon–fluorine molar bond enthalpy (E_m = 484 kJ mol^{-1}) is higher than that for carbon–chlorine (E_m = 338 kJ mol^{-1}) and the other carbon–halogen bonds so that electrochemical defluorination of compounds **2** is not expected. A near analogy for the carbon–halogen bond cleavage found here is to be seen with systems based on benzonitrile. The kinetics of fragmentation of 4-chlorobenzonitrile have been determined by an indirect electrochemical technique. The radical-anion intermediate fragments rapidly, equation (1) has E^0 = −2.08 V *vs* SCE and equation (2) has a rate constant of 1.58 × 10^8 s^{-1} in DMF.[10] By contrast, 4-fluorobenzonitrile radical-anion is sufficiently stable in DMF for its ESR spectrum to be recorded.[11]

1,5-Diphenyltetrazole shows an irreversible reduction peak on cyclic voltammetry with E_p = −2.1 V *vs* SCE and the halogen derivatives **2** show irreversible reduction at less negative potentials. In parallel to the case of halogenobenzonitriles, the carbon–fluorine bond will remain intact in the radical-anions derived from the series of diphenyltetrazoles **2** (X=Cl, Br, I) and the second carbon–halogen bond will cleave in preference.

Carbon–fluorine bonds can undergo electrochemical cleavage at sufficiently negative potentials. Thus, fluorobenzene undergoes irreversible reduction at a mercury cathode in DMF with $E_{1/2}$ = −2.97 V *vs.* SCE at 30 °C.[12] Evidence for the bond cleavage comes from reaction of fluorobenzene with solvated electrons in liquid ammonia where the so-formed phenyl radical has been trapped by reaction with acetone enolate ions.[3] Phenylacetone is isolated from this reaction.

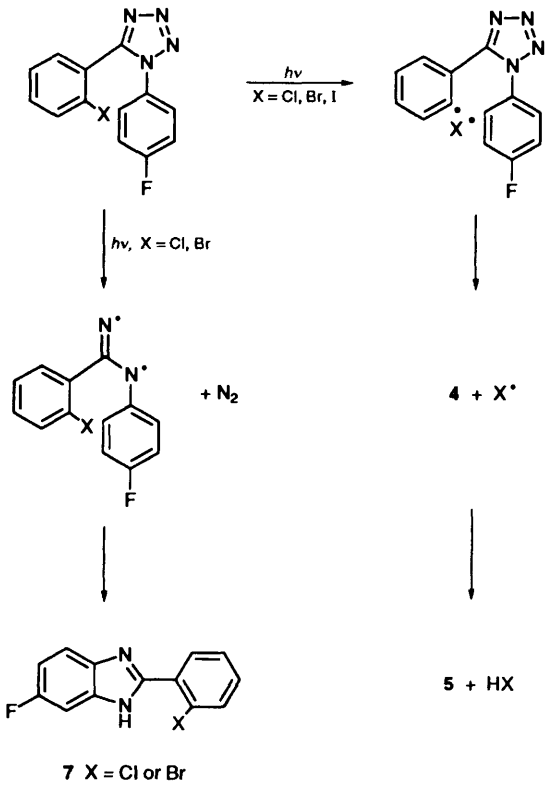
Electrochemical reduction of diphenyltetrazole and of 7-fluorotetrazolo[1,5-*f*]phenanthridine **5** occurs with cleavage of the tetrazole ring and loss of nitrogen.

Electrochemical reduction of 2 (X = Cl or Br) in acetonitrile led to three principal products characterised by the ^{19}F NMR signals at δ −32.8, −46.1 and −47.8 ppm from trifluoromethylbenzene as external standard. These products have been separated and identified. A fourth product with a ^{19}F NMR signal at δ − 42.5 ppm was present in too small an amount to allow purification but it has been converted into the compound with a signal at −47.8 ppm. Relative yields of these products were determined by integrating the spectra obtained from the total reaction mixture from reductions carried out to 80–90% completion. Sequences in the formation of these compounds are shown in Scheme 1.



Scheme 1 Electrochemical reduction

Crystallization of the reaction mixtures afforded 7-fluorotetrazolo[1,5-*f*]phenanthridine **5** with a ^{19}F NMR signal at −47.8 ppm. Pure samples of this material were most conveniently obtained from photolysis of the iodo compound **2** (X=I) discussed later. Accurate mass spectrometry indicated the expected molecular formula and the ^{1}H NMR spectrum is interpreted (see Experimental section) in terms of structure **5**. The UV spectrum shows a number of discrete vibrational bands as expected for a condensed aromatic structure.



Scheme 2 Photochemical reactions

The ^{19}F NMR signal at δ −46.1 was confirmed as due to 1-(4-fluorophenyl)-5-phenyltetrazole 2 (X=H) by comparison of the spectrum with that from an authentic sample.

The more soluble material from fractional crystallization of reaction mixtures was collected and separated by thin-layer chromatography on silica gel eluting with chloroform–2% methanol. A pure sample of the component with ^{19}F NMR signal at −32.8 ppm was obtained. Accurate mass spectrometry indicated the molecular formula $C_{13}H_9FN_4$. Analysis of the ^{1}H NMR spectrum (Fig. 1) on the basis of double-irradiation experiments carried out on each group of lines in turn, indicates that this component must be the dihydro derivative **6** of 7-fluorotetrazolo[1,5-*f*]phenanthridine.

This material shows two signals in the range 2.9–3.9 due to two methylene groups. The signals are coupled to each other with J = 9.6 Hz and are due to a CH_2CH_2 system. These two methylene groups are associated with the fluorine-substituted ring because each line of the two triplets is itself a doublet and this latter coupling is not associated with any other proton resonance. The doublet at δ 6.62 is not coupled to any other signal in the ^{1}H NMR spectrum, so the coupling with J = 12.5 Hz is due to fluorine and the proton giving rise to this signal is attached to an alkene bond. All five protons so far discussed can be accommodated in the cyclohexadiene ring of structure **6**. The remaining signals at δ 7.55–8.7 are due to four protons, each coupled to others in the group. None of these protons is coupled to fluorine. The four protons are attached to an *ortho*-disubstituted benzene ring and can be accommodated as H^9–H^{12} of the structure **6**.

Reaction product **6** arises from the radical intermediate **4** by further reduction to the carbanion and then protonation. The first formed dihydro compound, which may have an arrangement of alkene bonds different to that shown, will rearrange to the most stable form. Rearrangement can be either in a process catalysed by base formed as a consequence of the protonation steps, or in a series of [1,5]-sigmatropic rearrangements.

Compound **6** is slowly transformed into **5** by reaction with

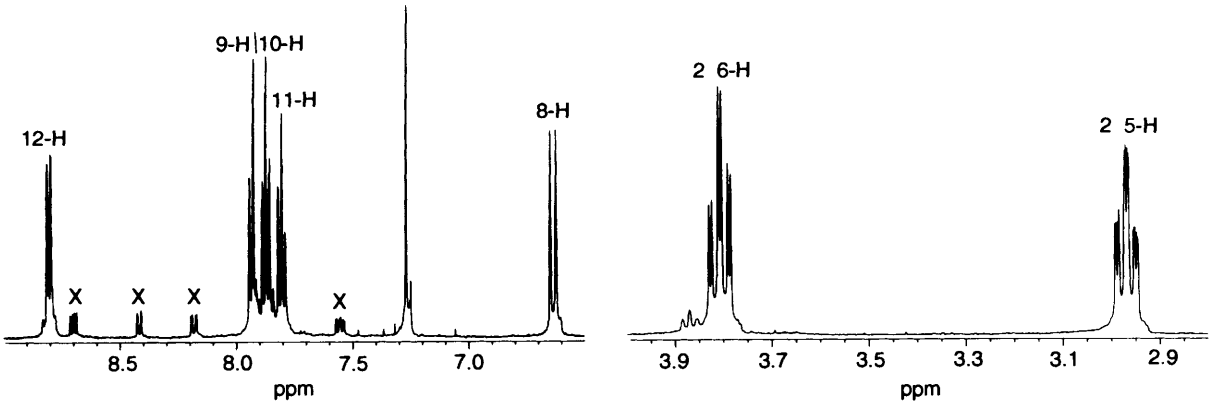


Fig. 1 ^{1}H NMR spectrum of compound **6** with δ_F −32.8 ppm. Resonances labelled x are due to contamination with 7-fluorotetrazolo-[1,5-*f*]phenanthridine.

Table 1 Product yields from electrochemical reduction of compounds **2**, determined by integration of the ^{19}F NMR spectrum

	% Yield			
X	**2** (X=H)	**5**	**6**	Unknown[a] (δ_F −42.5 ppm)
Cl	10	63	22	5
Br	39	50	9	2
I	31	66	0	3

[a] A cyclohexadiene isomer of **6**

2,3-dichlorodicyano-1,4-benzoquinone in benzene, following the use of ^{1}H and ^{19}F NMR spectroscopy. The compound with a ^{19}F NMR signal at −47.8 ppm was obtained as an enriched mixture with **5** and **6** by fractional crystallization of the total products. Reaction of this mixture with 2,3-dichlorodicyano-1,4-benzoquinone led to the slow transformation of both this compound with δ_F −47.8 ppm and **6** into **5**, followed by NMR spectroscopy. Thus, the compound is an alkene isomer of **6**. Electrochemical reduction of **2** (X=I) yielded only **2** (X = H) and **5**.

Product ratios from reduction of the three halogeno compounds **2** are compared in Table 1. These compounds arise according to Scheme 1. The ratio of total cyclization products to hydrogen abstraction product derived from radical **3** is, of course, **5** + **6** + compound with δ_F −47.8 ppm): **2** (X=H). Differences in the value of this ratio are detected along the series of three precursor compounds for this radical. They arise because of the relative rates of bond cleavage in the radical-anion to give **3**. When X = Cl, the bond cleavage reaction is sufficiently slow that the radical-ion is able to diffuse from the electrode surface. The σ radical **3**, when formed, must then diffuse either back to the electrode or towards another radical-anion in order to accept a further electron. Cyclization to **4** can occur during the time required for these diffusion steps.

The ratio of cyclization products to hydrogen abstraction product is almost identical within experimental error, for the compounds with X = Br and I. In another quantitative study of the electrochemical cyclization,[5] we observed distinctly more cyclization from the bromo substrate than from the iodo substrate. For the compounds in Table 1, when X = Br and I, bond cleavage of the radical-anion must be very fast and occur close to the electrode. Thus, in both these cases the ratio of cyclized products to **2** (X=H) derived from the σ radical **3** is determined by the relative rates of intramolecular substitution and of further electron transfer from the electrode with no diffusion step involved.

There is a clear trend in an increased yield of the dihydro compound **6** along the series I, Br, Cl. The reduction of these substrates is necessarily carried out at different electrode potentials with the chloro compound requiring the most negative potential and this change of potential will increase the rate for further reduction of the radical intermediate **4**.

Photochemical Reaction.—The tetrazoles **2** (X=Cl, Br or I) show a strong absorption maximum in the region 220–230 nm. Irradiation of these compounds in acetonitrile using a high-pressure Hg lamp resulted in the disappearance of starting material, and the reaction was followed by ^{19}F NMR spectroscopy. The iodo compound yielded only one product which was identified as 7-fluorotetrazolo[1,5-*f*]phenanthridine **5**.

Irradiation of the chloro compound yielded two products, one of which was identified as the tetrazolophenanthridine. The second product showed a single broad resonance in its ^{19}F NMR spectrum and this resonance was transformed into two sharp signals at δ −55.1 and −57.4 ppm after the sample had been shaken with dilute alkali. An enriched sample of this product, obtained by fractional crystallization, showed a molecular ion of composition $C_{13}H_8ClFN_2$. This second product was identified as 2-(2-chlorophenyl)-5-fluorobenzimidazole **7** by comparison of spectral data with the ^{19}F NMR spectrum from a sample prepared by reaction between 4-fluoro-*o*-phenylenediamine and 2-chlorobenzoic acid. Scheme 2 illustrates the pathways for these photoproducts.

In the absence of any proton catalyst, tautomerism between the two NH forms of the imidazole ring is slow on the NMR time scale. Consequently, pure compound **7** shows two ^{19}F NMR signals. A trace of hydrogen halide, formed during the photochemical reaction to give **5**, can catalyse the tautomerism and this double signal collapses to a broad singlet.

Irradiation of the bromotetrazole 2 (X=Br) also yielded **5** and **7**. In addition, the ^{19}F NMR spectrum indicated formation of an unknown compound with δ −49.2. It proved impossible to obtain a pure sample of this latter compound for identification.

The product yields summarized in Table 2 are taken from reactions carried to *ca.* 90% completion. They clearly indicate a competition between two major reaction pathways from the excited state of **2** (X=Cl, Br or I). Cleavage of the C–X bond leads eventually to cyclization and the formation of 7-fluorotetrazolo[1,5-*f*]phenanthridine **5**, while cleavage of the tetrazole ring with loss of nitrogen leads eventually to the benzimidazole **7**. This latter reaction is well established for diphenyltetrazoles.[8] The reactions are summarized in Scheme 2.

In contrast to the electrochemical reaction, photochemical cleavage of the C–X bond leads only to cyclization of the σ-

Table 2 Product yields from photochemical reaction of compounds **2**, determined by ^{19}F NMR spectroscopy

	% Yield		
X	**5**	**7**	Unknown (δ_F −49.2 ppm)
Cl	30	67	1
Br	54	25	21
I	100	0	0

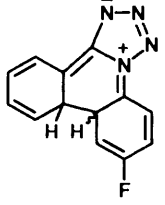
Table 3 ^{19}F NMR chemical shift (ppm from $PhCF_3$)

Compound	ppm	Compound	ppm
1 (X=H)	−54.8	**5**	−47.8
1 (X=Cl, Br or I)	−54.3	**6**	−32.8
2 (X=H)	−46.1	**7** (X=Cl)	−55.1 and −57.4
2 (X=Cl, Br or I)	−46.8	**9**	−55.7
		10	−49.7

radical intermediate with no 1-(4-fluorophenyl)-5-phenyltetrazole **2** (X=H) being formed. The latter compound is not itself photostable but will undergo loss of nitrogen and conversion into **7**. However, no intermediate with the characteristic NMR signal of **2** (X=H) can be detected even during the early stages of the photoreaction when it is screened from UV radiation by the high concentration of starting material.

Carbon–halogen bond cleavage becomes the dominant reaction as the bond strength decreases from C–Cl to C–I and this must be a photochemically induced bond homolysis. The alternative process of photocyclization of **2** to the zwitterion **8**, followed by loss of the hydrogen halide, implies that the rate-determining cyclization is little dependent on the nature of the halogen. A consequence of this alternative reaction pathway is that the product ratio of **5** to **7** would be little dependent on the halogen atom, which is not the observed case. The zwitterion **8** is a high-energy species because its formation involves both charge separation and the loss of benzene resonance energy and it is, therefore, excluded as a reaction intermediate.

The photocleavage of the tetrazole ring has an electrochemical parallel. Electrochemical reduction of 1,5-diphenyltetrazole affords *N*-phenylbenzamidine and reduction of **5** gives the related amidine **9**. Reduction of **5** with lithium aluminium hydride gave the amidine **9**, together with 2-fluorophenanthridine **10** and its 1,2-dihydro derivative. The dihydro derivative was converted into **10** during work-up of the reaction mixture.



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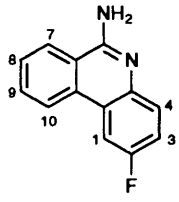

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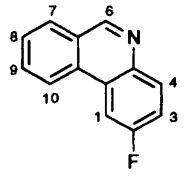

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Experimental

NMR spectra ($CDCl_3$ solvent) were recorded with a 500 MHz General Electric instrument. The ^{19}F NMR external reference was trifluoromethylbenzene. The recorded shifts are collected in Table 3. ^1H–^1H and ^1H–^{19}F coupling constants are in Hz. A VG mass spectrometer was used. HPLC grade acetonitrile was used without further purification. Dimethylformamide was kept over anhydrous copper sulphate, decanted and distilled under nitrogen at 30 mmHg. Sodium azide was dried *in vacuo* before use.

Benzanilides.—The appropriate 2-halogenobenzoyl chloride (0.127 mol) was slowly added to a stirred solution of 4-fluoroaniline (0.129 mol) in pyridine (30 cm^3) cooled to 0 °C. After 12 h, the mixture was poured onto ice and hydrochloric acid (3 mol dm^{-3}; 150 cm^3). The precipitated amide was collected and crystallized from ethanol: *2-chloro-4'-fluorobenzanilide*, large needles, m.p. 121–123 °C (Found: C, 62.6; H, 3.4; N, 5.5. $C_{13}H_9ClFNO$ requires C, 62.5 H, 3.6; N, 5.6%), ν_{CO}(KBr)/cm^{-1} 1647, M^+ 249 and 251; *2-bromo-4'-fluorobenzanilide*, large needles, m.p. 124–125 °C (Found: C, 52.9; H, 3.2; N, 4.6. $C_{13}H_9BrFNO$ requires C, 53.0; H, 3.1; N, 4.8%), ν_{CO}(KBr)/cm^{-1} 1651, M^+ 293 and 295; *4'-fluoro-2-iodobenzanilide*, needles, m.p. 139–140 °C (Found: C, 45.7; H, 2.7; N, 4.3. $C_{13}H_9FINO$ requires C, 45.8; H, 2.7; N, 4.1%), ν_{CO}(KBr)/cm^{-1} 1651, M^+ 341; 4'-fluorobenzanilide, m.p. 186–187 °C (lit.,[13] m.p. 186–188 °C).

Tetrazoles.—The appropriate benzanilide (0.085 mol) and a slight excess of phosphorus pentachloride (0.093 mol) were powdered together and heated in an oil-bath at 60–70 °C for 1 h under nitrogen. Phosphorus oxychloride was then removed under reduced pressure to leave a residue of the imido chloride. This was dissolved in dry dimethylformamide (90 cm^3) and added dropwise to a stirred suspension of an excess of dry sodium azide (0.170 mol) in dry dimethylformamide (85 cm^3) over 1 h at 26 °C. The mixture was stirred overnight at room temperature and then diluted with water (200 cm^3) and left at 0 °C. The precipitated tetrazole was collected, washed with water and recrystallised from ethanol (60–80°%): *5-(2-chlorophenyl)-1-(4-fluorophenyl)tetrazole*, needles, m.p. 104–106 °C (Found: C, 57.0; H, 2.7; N, 20.4. $C_{13}H_8ClFN_4$ requires C, 56.8; H, 2.9; N, 20.4%), *m/z* (% abundance) 276 (0.5), 274 (1.5, M^+), 248 (45), 246 (100, M^+-N_2), 109 (70), 95 (21); *5-(2-bromophenyl)-1-(4-fluorophenyl)tetrazole*, needles, m.p. 124–126 °C (Found: C, 49.0; H, 2.5; N, 17.5. $C_{13}H_8BrFN_4$ requires C, 48.9; H, 2.5; N, 17.6%), *m/z* (% abundance) 320 (0.7), 318 (0.7, M^+), 292 (100), 290 (97, M^+-N_2), 185 (20) and 183 (23); *1-(4-fluorophenyl)-5-(2-iodophenyl)tetrazole*, needles, m.p. 135–137 °C (Found: C, 42.8; H, 2.1; N, 15.1. $C_{13}H_8FIN_4$ requires C, 42.7; H, 2.2; N, 15.3%), *m/z* (% abundance) 366 (15, M^+), 338 (100, M^+-N_2), 210 (35) and 109 (36); *1-(4-fluorophenyl)phenyltetrazole*, needles, m.p. 137–140 °F (Found: C, 65.0; H, 3.6; N, 23.5. $C_{13}H_9FN_4$ requires C, 65.0; H, 3.8; N, 23.3%), *m/z* (% abundance) 250 (52, M^+), 212 (100, $M^+ - N_2$), 109 (43), 105 (29) and 77 (42).

2-(2-Chlorophenyl)-5-fluorobenzimidazole. Fluoro-*o*-phenylenediamine (0.15 g, 0.01 mol) and 2-chlorobenzoic acid (1.88 g, 0.01 mol) were mixed to a paste with warm polyphosphoric acid (35 g) and the mixture kept at 250 °C for 5 h under nitrogen. After cooling to *ca.* 100 °C, the reaction mixture was poured into rapidly stirred water (100 cm^3) filtered and the filtrate neutralized to pH 8 with 50% sodium hydroxide. Excessive rise in temperature was prevented by addition of ice as necessary. The resulting slurry was filtered at *ca.* 50 °C and the product washed free of inorganic salts, dried and crystallized from ethanol. The *title compound* formed fine needles, m.p. 153–155 °C (M^+, 246.03600. $C_{13}H_8ClFN_2$ requires 246.03600); *m/z* (% abundance) 248 (30), 246 (100), 211 (12), 135 (8).

Electrochemical Reactions.—These reactions were carried out in an H-type cell with platinum anode, mercury pool cathode (area 7 cm^2) and a saturated calomel reference electrode. Supporting electrolyte and solvent were 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate in acetonitrile, unless otherwise stated. The anolyte contained the electrolyte solution. The catholyte was stirred and kept under nitrogen; its composition is specified for each experiment. Reactions were carried out at constant potential.

1,5-*Diphenyltetrazole.*—The electrolyte used was 0.1 mol dm^{-3} tetrapropylammonium fluoroborate in dimethylformamide. A solution of 1,5-diphenyltetrazole (0.46 g) in electrolyte (20 cm^3) was reduced at a cathode potential of −2.1 V *vs.* SCE. After 8 h, the current fell to a low value and 2 F mol^{-1} were consumed. Evaporation of the catholyte left a brown oil which was dissolved in dichloromethane (50 cm^3) and the solution washed with water to remove the electrolyte and dried (Na_2SO_4). The product was purified by TLC on silica gel, eluting with ether. *N*-Phenylbenzamidine was isolated from the principal band and crystallized from ether as colourless needles (0.11 g, 27%), m.p. 115–118 °C (lit.,[14] m.p. 115–118 °) (Found: C, 79.8; H, 6.1; N, 14.6. Calc. for $C_{13}H_{12}N_2$: C, 79.6; H, 6.2; N, 14.3%).

5-(2-*Chlorophenyl*)-1-(4-*fluorophenyl*)*tetrazole.* The title compound (50 mg) in electrolyte (15 cm^3) was reduced at a cathode potential of −1.86 V *vs.* SCE. After 7 min the current fell to a low value with passage of 1.1 F mol^{-1}. At the end of the reaction the solution turned green, presumably due to the more stable radical-anion of **5**. The reaction mixture was evaporated to dryness under reduced pressure and the residue dissolved in dichloromethane. The organic layer was collected, washed several times with water, dried (Na_2SO_4) and the solvent removed. Yields of products were determined by ^{19}F NMR spectroscopy. Compound **2** (X=H) was identified by comparison of its ^{19}F NMR spectrum with that of an authentic specimen. Crystallization from methanol afforded some **5** and separation of the more soluble material was achieved by TLC (see below).

When the reduction was continued with the passage of up to 2 F mol^{-1}, the yield of **5** fell and a new product with δ_F − 55.7 appeared. The new product was later identified as 6-amino-2-fluorophenanthridine **9** by comparison with the ^{19}F NMR spectrum of the material from reduction with lithium aluminium hydride.

5-(2-*Bromophenyl*)-1-(4-*fluorophenyl*)*tetrazole.*—The title compound (50 mg) in electrolyte (15 cm^3) was reduced at a cathode potential of −1.84 V *vs.* SCE. After 11 min the current fell to zero with passage of 0.96 F mol^{-1}. The mixture was worked up as for the previous example and relative yields of products determined by ^{19}F NMR spectroscopy.

1-(4-*Fluorophenyl*)-5-(2-*iodophenyl*)*tetrazole.*—The title compound (50 mg) in electrolyte (15 cm^3) was reduced at a cathode potential of −1.54 V *vs.* SCE. The current fell to zero after 5 min with passage of 0.9 F mol^{-1}. The mixture was worked up as before and relative yields of products determined by ^{19}F NMR spectroscopy.

Photochemical Reaction.—A solution of the tetrazole (200 mg) in acetonitrile (150 cm^3) was irradiated for 1.5 h using a Hanau 400 W mercury lamp with water-cooled quartz-immersion well. Samples (3 cm^3) of the solution were removed at intervals, evaporated under reduced pressure, the residue dissolved in $CDCl_3$ and the components analysed by ^{19}F NMR spectroscopy.

7-*Fluorotetrazolo*[1,5-*f*]*phenanthridine* **5.**—The title compound was conveniently isolated by crystallization of the reaction product from the photolysis of **2** (X=I). Crystallization from methanol afforded the *title compound* (92 %) as needles, m.p. 233–235 °C (Found: C, 65.7; H, 3.3; N, 23.2. $C_{13}H_7FN_4$ requires C, 65.5; 3.0; N, 23.5%); *m/z* (% abundance) 238 (18, M^+) and 210 (100, M^+-N_2); δ_H 8.82 (4-H, $J_{4,5}$ 8.03), 8.72 (5-H, $J_{5,6}$ 9.3, $J_{H,F}$ = 5.0); 8.42 (9-H, $J_{9,10}$ 8.1), 8.19 (8-H, $J_{H,F}$ 9.7, $J_{6,8}$ 2.5), 7.94 (11-H, $J_{11,12} = J_{10,11}$ 8.1), 7.87 (10-H, $J_{10,11} = J_{9,10}$ 8.1) and 7.57 (H_6, $J_{6,5} = J_{HF}$ 9.3, $J_{6,8}$ 2.5).

Isolation of the Dihydro Derivatives of **5.**—In addition to starting material and 1-(4-fluorophenyl)-5-phenyltetrazole, the reaction mixture from electrochemical reduction of the chloro compound contains **5**, **6** and the unknown with δ_F −42.5 ppm. Separation of these materials was monitored by ^{19}F NMR spectroscopy. The mixture of five components was subjected to TLC on silica gel, eluting with ether–light petroleum (b.p. 40–60 °C) (1:1). This afforded three bands: R_f 0.43, identified as **2** (X=H); R_f 0.31, identified as **2** (R=Cl); R_f 0.15 which was a mixture of **5**, **6** and the unknown. This mixture of three components was separated by TLC on silica gel eluting with chloroform–methanol (98:2). Two bands were obtained: R_f 0.44, identified as **5**; R_f 0.34 which contained 85% of compound **6**, 9% of compound **5** and 6% of the unknown with δ_F − 42.5 ppm. The major *component* **6** (M^+, 240.0801. $C_{13}H_9FN_4$ requires 240.0811) showed *m/z* (% abundance) 240 (M^+, 15), 212 (M^+-N_2, 75) and 211 (100); δ_H 8.80 (12-H, $J_{11,12}$ 8.1), 7.92 (9-H, $J_{9,10}$ 8.1), 7.87 (10-H, $J_{9,10} = J_{10,11}$ 8.1), 7.82 (11-H, $J_{11.12} = J_{10,11}$ 8.1), 6.64, (8-H, J_{HF} 12.5), 3.82 (2 × 6-H, $J_{5,6}$ 9.6, J_{HF} 1.2) and 2.97 (2 × 5-H, $J_{5,6}$ 9.6, J_{HF} 1.8).

Compound **6** (4 mg) and 2,3-dichlorodicyano-1,4-benzoquinone (7 mg) were dissolved in [$^2H_6$]benzene (1 cm^3) and heated at 50 °C. ^{19}F and ^1H NMR spectroscopy were used to observe the conversion of **6** into 9-fluorotetrazolo[1,4-*f*]-phenanthridine **5** over 48 h.

A mixture of the unknown with δ_F −42.5 ppm containing **5** and **6** was obtained by fractional crystallization of the total products from reduction of the chloro compound. Dehydrogenation of this mixture as above caused the conversion of both the unknown and **6** into **5**, followed by ^{19}F NMR spectroscopy.

2-*Fluorophenanthridine* **10.**—7-Fluorotetrazolo[1,5-*f*]phenanthridine (200 mg, 1 mmol) was dissolved in dry tetrahydrofuran (30 cm^3) and added dropwise to a stirred suspension of lithium aluminium hydride (500 mg, 0.01 mol) in tetrahydrofuran (20 cm^3). The mixture was refluxed for 48 h under nitrogen and then cooled in ice during the cautious addition of water. The products were extracted into ether and the solution washed with water, dried (Na_2SO_4) and evaporated. ^{19}F NMR spectroscopy indicated the presence of three compounds later identified as 2-fluorophenanthridine (7%), 2-fluoro-5,6-dihydrophenanthridine (50%) and 2-fluorophenanthridin-6-amine (43%). Chromatography on silica gel plates eluting with ether showed only two spots. Yields of products isolated indicate that, during chromatography, the 5,6-dihydrophenanthridine is rapidly oxidized by air to 2-fluorophenanthridine. The dihydro compound could not be isolated. Separation by TLC afforded: 2-*fluorophenanthridin*-6-*amine* **9** (M^+, 212.0752. $C_{13}H_9FN_2$ requires 212.0750), R_f 0.09; δ_H 8.41 (7-H, $J_{7,8}$ 8.2), 7.99 (1-H, $J_{H,F}$ 10.1, $J_{1,3}$ 2.8), 7.93 (10-H, $J_{9,10}$ 8.2), 7.82 (9-H, $J_{8,9} = J_{9,10}$ 8.2), 7.68 (8-H, $J_{7,8} = J_{8,9}$ 8.2), 7.32 (3-H, $J_{H,F} = J_{3,4}$ 8.3, $J_{1,3}$ 2.8), 5.40 (2 H, of NH_2, br s); 2-*fluorophenanthridine* (M^+, 197.0635. $C_{13}H_8FN$ requires 197.0641), R_f 0.38; δ_H 9.25 (6-H, s), 8.5 (7-H, $J_{7,8}$ 8.1), 8.18 (4-H + 1-H, m), 8.07 (10-H, $J_{9,10}$ 8.1), 7.89 (8-H, $J_{8,9} = J_{7,8}$ 8.1), 7.76 (9-H, $J_{8,9} = J_{9,10}$ 8.1) and 7.49 (3-H, $J_{3,4} = J_{HF}$ 8.8).

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