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Regioselectivity in the Intramolecular Substitution Reactions of Electrochemically and Photochemically Generated Aryl Radicals with Adjacent Pyridine and Quinoline Rings. A Comparison between these Reactions and Related Processes Involving Tributyltin Hydride

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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Cleavage of the carbon–halogen bond in 1-(3-pyridinyl)- and 1-(3-quinolinyl)-5-(1-halogenophenyl)tetrazoles leads to a σ-radical which undergoes a cyclization reaction onto the adjacent heterocyclic ring. Bond cleavage is effected both by electrochemical reduction and by photolysis. Yields of cyclized products formed in the two types of reaction are compared. The relative advantages of the electrochemical generation of an aryl σ-radical from aryl halides over reaction of the same substrate with tributyltin hydride and a radical initiator are discussed.

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. This intermediate decomposes to generate a σ-radical and a halide ion.[1–5] Aryl radicals so formed can undergo rapid intramolecular substitution onto an adjacent benzene ring and examples of electrochemically initiated ring-closure processes have been given.[6–14] Some of these electrochemically initiated reactions can be carried out at a mild-steel cathode in an undivided cell using a sacrificial magnesium anode.[6] Ring closure onto an adjacent alkene bond can also be achieved by the electrochemical process.[15]

In previous papers[13,14] we have compared the advantages of the electrochemical process with those of a related photochemically initiated ring closure. The photochemical reaction may involve aryl radicals generated by carbon–halogen bond homolysis, but another recognised mechanism involves an initial electrocyclic ring closure, followed by loss of hydrogen halide.[16] This paper extends comparison of the two reactions to examples of cyclization onto a pyridine or a quinoline ring. Aryl radicals have also been generated from aryl halides by the action of tributyltin hydride and a radical initiator.[17,18] Intramolecular cyclization processes involving radicals generated in this way reacting with an adjacent benzene ring are known.[19,20] It was interesting therefore to compare the relative advantages, for achieving a specific target synthesis, of the electrochemical cyclization process, the photochemical process and this related chemical reaction.

Reactions of the pyridine and quinoline derivatives **2a–c** are examined here. The tetrazole substrates are conveniently prepared from the corresponding benzamides **1** by conversion into the imido chloride and then reaction with sodium azide. The tetrazole framework serves both to hold the reacting aryl rings in adjacent positions and as a synthon for the –CH=N– function into which it can be converted by further reduction.[14] A fluorine substituent was placed on one benzene ring so as to aid quantitative analysis of reaction mixtures by ^{19}F NMR spectroscopy. 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 also the other

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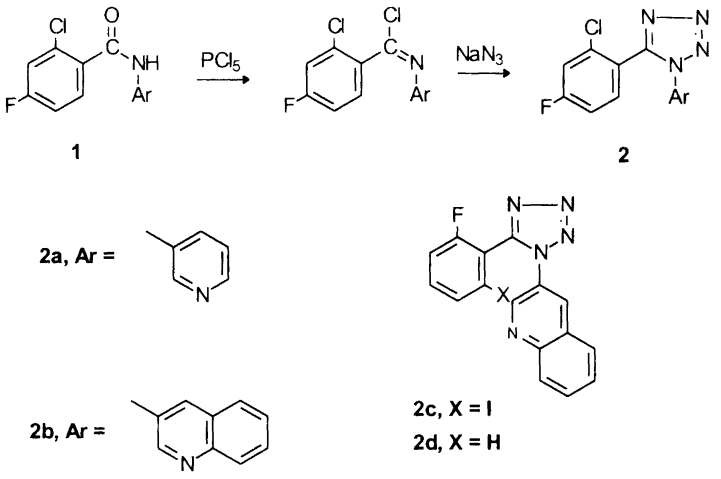


carbon–halogen bonds. This ensures that homolysis of the carbon–fluorine bond will not occur in preference to cleavage of other carbon–halogen bonds. As a precaution, runs were carried out to less than 95% completion.

Electrochemical and photochemical reactions

The yields of products from electrochemical and photochemical reactions are collected in Table 1.

Pyridine derivatives. Reduction of the chloro compound **2a** in acetonitrile at a mercury cathode gave three products. The product **6** derived by replacement of the chlorine substituent by hydrogen was identified by comparison of the ^{19}F NMR signal with an authentic specimen. Separation of the mixture by chromatography on silica gel and then fractional crystallisation afforded pure samples of the other two fluorine-containing compounds. These were identified as **4** and **5** by analysis of their ^{1}H NMR spectra. Spectral analysis was based upon double irradiation experiments carried out on each group of lines. Compound **4** is easily identified because of the singlet at δ 10.06 which is assigned to 5-H. No singlet is found in the proton spectrum of **5**. The remaining two protons 7-H and 8-H on the pyridine ring of **4** give rise to signals at δ 9.06 and δ 8.26, each of which is a doublet. Signals due to the three pyridine ring protons of **5** are also easily identified in the NMR spectrum with 7-H at δ 9.05 coupled to 6-H at δ 7.88 which is also coupled to 5-H at δ 8.95.

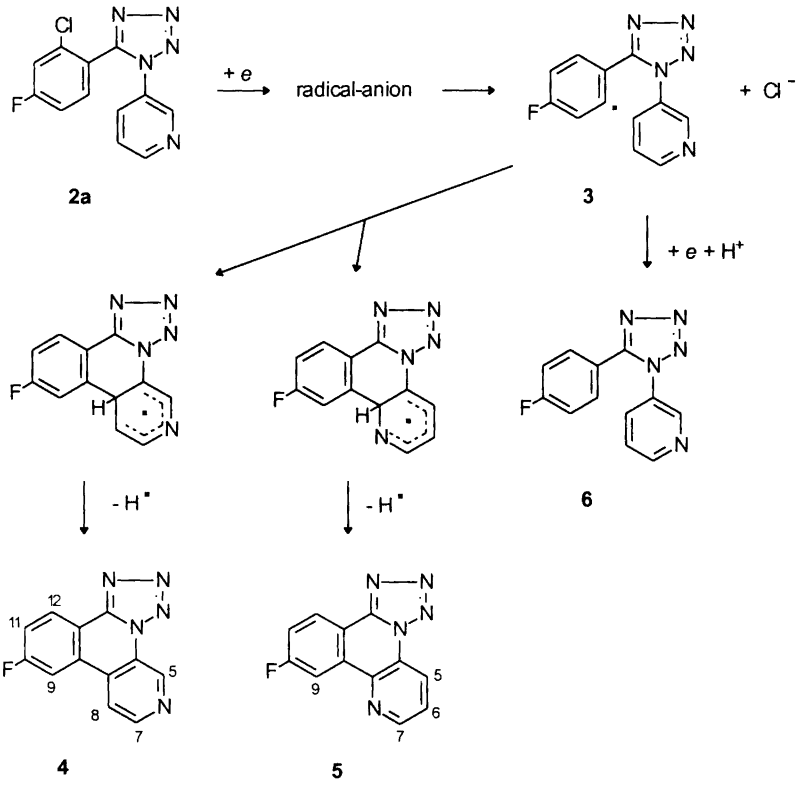
Table 1. Relative yields of product from the electrochemical and photochemical reactions in acetonitrile, determined by integration of the ^{19}F NMR spectrum.

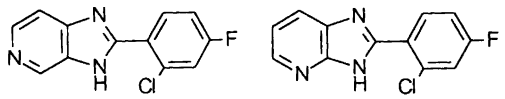
Substrate	Reaction type	% Yield (product)		
2a	Electrochemical	35 (**4**)	54 (**5**)	11 (**6**)
	Photochemical	28 (**4**)	72 (**5**)	0 (**6**)
2b	Electrochemical	31 (**9**)	58 (**10**)	11 (**11**)
	Photochemical	No reaction after 72 h		
2c	Electrochemical	29 (**12**)	50 (**13**)	21 (**2d**)
	Photochemical	40 (**12**)	60 (**13**)	0 (**2d**)

Compound **2a** shows a UV spectrum with λ_{max} 260 nm. Irradiation in acetonitrile caused its conversion into a mixture of **4** and **5** over a period of 15 h. The characteristic photochemical reaction of diphenyltetrazoles is loss of dinitrogen followed by cyclization of the resulting diradical to yield an imidazole derivative.[14,21,22] The absence of this reaction path for the phenylpyridinyltetrazoles was established as follows. The two possible products **7** and **8** were both synthesised by reaction between the appropriate diaminopyridine and 2-chloro-4-fluorobenzoic acid. The ^{19}F NMR signals due to these compounds were not found in the spectrum of the crude photolysis product. Thus the excited state of **2a** does not have sufficient energy to react by tetrazole ring cleavage which contrasts with the photochemistry of halogen-substituted 1,5-diphenyltetrazoles (λ_{max} 232 nm) for which the excited state energy is of higher value.[14]

None of the product from replacement of chlorine by hydrogen is found in the photochemical reaction of **2a**, compared with 11% from the electrochemical process. This result illustrates the further reduction of radical intermediates to carbanions at a cathode as a process which is in competition with radical ring closure reaction. In both cyclization processes substitution occurs predominantly at the 2-position of the pyridine ring which is in agreement with results from intermolecular phenyl radical substitution processes on pyridine.[23]

Quinoline derivatives. Electrochemical reduction of **2b** afforded three products, none of which was the compound from replacement of chlorine by hydrogen. The two principal products were separated by chromatography on silica gel and identified by ^{1}H NMR spectroscopy as the two condensed ring compounds, **9** and **10**. The third product **11** could not be isolated in a pure state It was recognised as a dihydro derivative of **10** because, on warming the total reaction mixture with 2,3-dichlorodicyano-1,4-benzoquinone, the ^{19}F NMR signal





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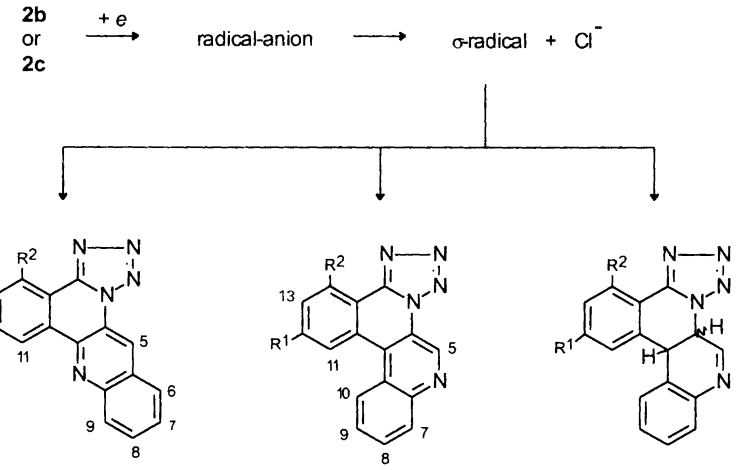
at δ −41.9 disappeared while the signal at δ −41.0 was simultaneously enhanced. Diagram **11** illustrates one possible dihydrobenzene structure, but the two hydrogen atoms removed by reaction with dichlorodicyanobenzoquinone have not been firmly located.

Assignment of ^{1}H NMR resonances for compounds **9** and **10** proceeded as follows. Both show a one-proton singlet due to 5-H on the quinoline ring. The signals due to the three protons on the fluorine-substituted ring are easily distinguished for each compound because of the coupling to fluorine and to hydrogen. The resonances due to the four remaining protons on the quinoline ring can then be identified for each compound. The two



9, R^1 = F, R^2 = H
12, R^1 = H, R^2 = F

10, R^1 = F, R^2 = H
13, R^1 = H, R^2 = F

11, R^1 = F, R^2 = H

compounds were distinguished by carrying out NOE experiments with irradiation at the signal corresponding to 5-H. Enhancement of the signal due to one of the other protons on the quinoline ring was observed for **9** but not for **10**.

Electrochemical reduction of the iodo compound **2c** yielded three products. One of these was identified as **2d** formed through replacement of iodine by hydrogen by comparison of the ^{19}F NMR signal with that from an authentic specimen. It arises by further reduction of the σ-radical to a carbanion that is then protonated. The other two products were the only compounds formed by photochemical reaction of the starting iodo compound. They were isolated by chromatography of the photochemical reaction mixture and identified as the two cyclization products **12** and **13** by analysis of their ^1H NMR spectra. Each compound shows a one-proton singlet due to 5-H and, in NOE experiments with irradiation at the frequency corresponding to this signal, only with compound **12** was enhancement observed of the signal due to one of the other protons on the quinoline ring.

Product distribution between cyclization and replacement of the halogen atom by hydrogen in these and related electrochemical reactions is determined by the rate of cleavage of the carbon–halogen bond in the initially formed radical-anion. When this rate is faster, the σ-radical is formed closer to the electrode so that back diffusion to the electrode and further reduction can compete with the fast ring closure process. Bond cleavage rates depend on the energy level of the unpaired electron in the radical-anion and also on the carbon–halogen bond strength; thus that the carbon–iodine bond in **2c** cleaves faster than the carbon–chlorine bond in **2b**.

The chloro compound **2b** underwent no photochemical reaction during irradiation for 72 h. This compound shows a long wavelength absorption with λ_{max} 319 nm, so the excited state energy must be equal to or less than 375 kJ mol^{-1}, which is lower than the carbon–chlorine bond energy (397 kJ mol^{-1}), accounting for the observed lack of reactivity. In contrast, the iodo compound **2c** did undergo the cyclization process during irradiation, as expected, because the carbon–iodine bond energy (268 kJ mol^{-1}) is less than the excited state energy for the system.

Radical substitution at the 4-position of the quinoline ring is favoured in all the above cases. This observation is in agreement with studies on the reaction between quinoline and phenyl radicals generated by decomposition of dibenzoyl peroxide. Substitution occurs at any position and all seven possible monosubstitution products are formed with 8-phenylquinoline predominating. 4-Substitution predominates over 2-substitution.[24,25]

Reactions using tributyltin hydride. In a previous paper the electrochemical and photochemical cyclization reactions of 1-(4-fluorophenyl)-5-(2-halogenophenyl)tetrazoles **14** were examined. Reaction using tributyltin hydride involves a tributyltin radical generated using a radical initiator. Tributyltin radicals abstract halogen from the carbon–halogen bond yielding the same phenyl σ-radical as is formed electrochemically. The same range of products is found from these reactions as obtained by the electrochemical process[14] and in yields summarised in Table 2. One disadvantage of the tributyltin hydride reaction is that the carbon–chlorine bond is virtually unreactive. Mostly starting material was recovered after 72 h reflux with a tenfold excess of tributyltin hydride.

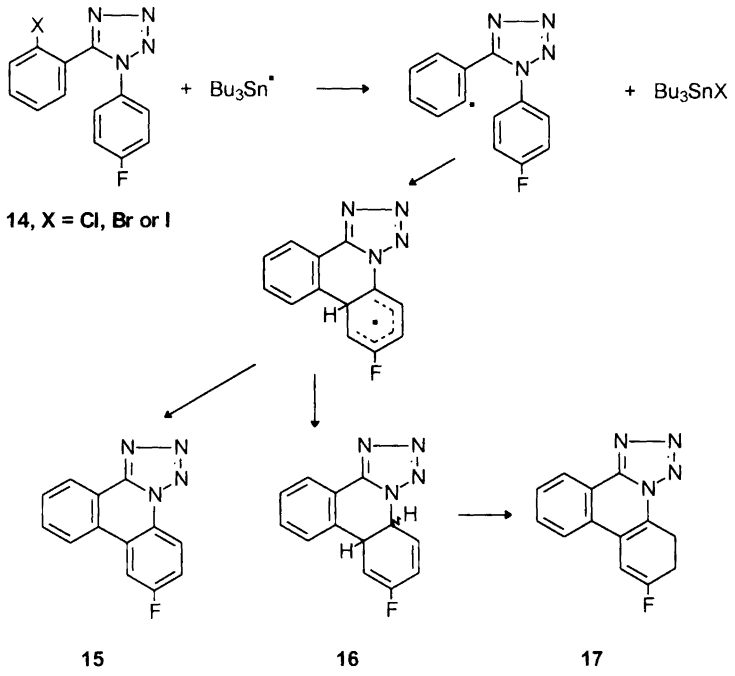


Table 2. Product yields from reaction with tributyltin hydride determined by ^{19}F NMR spectrometry using data from Ref. 5 for peak identification. Unreacted starting material accounts for the deficiency from 100%.

Substrate **14**, X=	Product (% yield)			
	14, X=H	**15**	**16**	**17**
Cl	0	8	1	0
Br	9	52	33	6
I	6	56	24	10

The carbon–bromine and carbon–iodine bonds react more readily.

This lack of reactivity of the carbon–chlorine bond towards tributyltin hydride was also observed for **2b**. The related iodo compound **2c** reacted readily to give cyclization products **13** (30%), **12** (22%) together with a high proportion of **2d** (48%) formed by replacement of the halogen atom by hydrogen. Cyclization occurs principally at the 4-position of the quinoline ring as for the electrochemical and the photochemical reaction.

Conclusions. Electrochemical cyclization has the advantage over the reaction initiated with tributyltin hydride in that it can be applied to the chloro compounds. Photochemical initiation of reaction is dependent on the excited state energy being sufficient to cleave the carbon–halogen bond and the presence of other frangible groups in the substrate may lead to competing reactions. The electrochemical reactions described here were carried out at a mercury cathode. We have demonstrated[6] that this type of process can be carried out at a mild-steel cathode in an undivided cell using a sacrificial magnesium anode, and under these experimental conditions, the electrochemical process becomes an attractive carbon–carbon bond forming reaction.

Experimental

NMR spectra ($CDCl_3$ solvent) were recorded with a 500 MHz General Electric instrument. The ^{19}F NMR external reference was trifluoromethylbenzene and important ^{19}F chemical shifts are listed in Table 3. The ^1H NMR internal reference was tetramethylsilane. ^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.

Table 3. ^{19}F NMR chemical shifts determined using $PhCF_3$ as external standard.

Compound	δ_F	Compound	δ_F
2a	−41.5	**7**	−44.0
2b	−41.5	**8**	−44.7
2c	−42.5	**9**	−40.6
2d	−47.7	**10**	−41.0
4	−40.3	**11**	−41.9
5	−40.8	**12**	−44.3
6	−43.7	**13**	−41.2

Benzamides. The appropriate benzoyl chloride (0.03 mol) was slowly added to a solution of the aminopyridine or aminoquinoline (0.03 mol) in pyridine (15 ml) and dichloromethane (50 ml). After 12 h, the mixture was poured into excess sodium hydroxide (100 ml, 2 M). The organic layer was collected, washed three times with water (50 ml), dried (Na_2SO_4) and the solvent removed. The residual amides were recrystallised from ethanol.

3-(2-Chloro-4-fluorobenzamido)pyridine, needles, m.p. 124–125 °C. Anal. Found: C 57.4; H 3.0; N 11.1. Calc. for $C_{12}H_8ClFN_2O$: C 57.5; H 3.2; N 11.1.

3-(4-Fluorobenzamido)pyridine, needles, m.p. 140–142 °C. Anal. Found: C 65.6; H 4.1: N 12.8. Calc. for $C_{12}H_9FN_2O$: C 65.5; H 4.2; N 12.7.

3-(2-Chloro-4-fluorobenzamido)quinoline, needles, m.p. 134–135 °C. Anal. Found: C 68.8; H 3.0; N 9.2. Calc. for $C_{16}H_{10}ClFN_2O$: C 68.9; H 3.3; N 9.3.

3-(4-Fluorobenzamido)quinoline, needles, m.p. 229–230 °C. Anal. Found: C 71.8; H 4.0; N 10.4. Calc. for $C_{16}H_{11}FN_2O$: C 72.1; H 4.2; N 10.5.

3-(2-Fluoro-6-iodobenzamido)quinoline, needles, m.p. 251–253 °C. Anal. Found: C 48.8; H 2.6; N 6.9. Calc. for $C_{16}H_{10}FN_2OI$: C 49.0; H 2.6; N 7.1.

3-(2-Fluorobenzamido)quinoline, needles, m.p. 155–156 °C. Anal. Found: C 71.9; H 4.0; N 10.4. Calc. for $C_{16}H_{11}FN_2O$: C 72.1; H 4.2; N 10.5.

Tetrazoles. The appropriate benzamide (0.012 mol) and a slight excess of phosphorus pentachloride (3.54 g., 0.017 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 (30 ml) and added dropwise to a stirred suspension of an excess of sodium azide (1.56 g., 0.024 mol) in dry dimethylformamide (20 ml) over 1 h at 26 °C. The mixture was stirred overnight at room temperature, diluted with water (50 ml) and left at 0 °C. The precipitated tetrazole was collected, washed with water and crystallized from ethanol (yields 60–80%).

5-(2-Chloro-4-fluorophenyl)-1-(pyridin-3-yl)tetrazole **2a**, needles, m.p. 159–161 °C. Anal. Found: C 52.3; H 2.4; N 25.2. Calc. for $C_{12}H_7ClFN_5$: C 52.3; H 2.6; N 25.4. MS EI: *m/z* (%) 277 (3), 275 (9, M^+), 249 (30), 247 (100, $M^+ - N_2$).

5-(4-Fluorophenyl)-1-(pyridin-3-yl)tetrazole **6**, needles, m.p. 120–121 °C. Anal. Found: C 59.4; H 3.3; N 28.9. Calc. for $C_{12}H_8FN_5$: C 59.7; H 3.3; N 29.0. MS EI: *m/z* (%) 241 (20, M^+), 213 (100, $M^+ - N_2$).

5-(2-Chloro-4-fluorophenyl)-1-(quinolin-3-yl)tetrazole, needles **2b**, m.p. 118–119 °C. Anal. Found: C 58.7; H 2.7; N 21.9. Calc. for $C_{16}H_9ClFN_5$: C 59.0; H 2.8; N 21.5. MS EI: *m/z* (%) 327 (3), 325 (8, M^+), 299 (33), 297 (100, $M^+ - N_2$).

5-(4-Fluorophenyl)-1-(quinolin-3-yl) tetrazole, needles, m.p. 122–124 °C. Anal. Found: C 65.6; H 3.3; N 23.9. Calc. for $C_{16}H_{10}FN_5$: C 66.0; H 3.5; N 24.0. MS EI: *m/z* (%) 291 (3, M^+), 263 (100, $M^+ - N_2$).

5-(2-Fluoro-6-iodophenyl)-1-(quinolin-3-yl) tetrazole **2c**, needles, m.p. 162–164 °C. Anal. Found: C 45.9; H 2.2; N 16.5. Calc. for $C_{16}H_9FIN_5$: C 46.1; H 2.2; N 16.8. MS EI: *m/z* (%) 414 (16, M^+), 389 (100, $M^+ - N_2$).

5-(2-Fluorophenyl)-1-(quinolin-3-yl) tetrazole **2d**, needles, m.p. 165–165 °C. Anal. Found: C 65.7; H 3.2; N 23.8. Calc. for $C_{16}H_{10}FN_5$: C 66.0; H 3.5; N 24.0. MS EI: *m/z* (%) 291 (10, M^+), 263 (100, $M^+ - N_2$).

2-(2-Chloro-4-fluorophenyl)-4-azabenzimidazole **8.** 2,3-Diaminopyridine (2.0 g) and 2-chloro-4-fluorobenzoic acid (3.54 g) were mixed with sufficient polyphosphoric acid (65 g) to give a paste. The mixture was heated at 250 °C for 4 h, cooled to 100 °C and poured into rapidly stirred water (150 ml). The product was precipitated by treating the mixture with 50% sodium hydroxide solution until the resulting slurry was alkaline to phenolphthalein indicator. The crude product was collected by filtration and crystallised from ethanol.

2-(2-Chloro-4-fluorophenyl)-4-azabenzimidazole **8** formed needles, m.p. 197–199 °C. HRMS: Calc. $C_{12}H_7ClFN_3$: 247.0313. Found: 247.0322.

2-(2-Chloro-4-fluorophenyl)-5-azabenzimidazole **7**. Prepared as for the previous example, the *title compound* formed needles, m.p. 220–224 °C. HRMS: Calc. $C_{12}H_7ClFN_3$ 247.0313. Found: 247.0318.

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 aqueous calomel reference electrode. Supporting electrolyte and solvent were 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate in acetonitrile. 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.

Reaction of 5-(2-chloro-4-fluorophenyl)-1-(pyridin-3-yl)-tetrazole. The title compound (50 mg) in electrolyte (15 cm^3) was reduced at a cathode potential of −1.8 V vs. SCE. After 9 min the current fell to a low value with the passage of 1.13 F mol^{-1}. The reaction mixture was evaporated to dryness under reduced pressure and the residue dissolved in dichloromethane. The organic layer was washed several times with water, dried (Na_2SO_4) and relative yields of **4**, **5**, and **6** determined (see Table 1). The products were separated by thin layer chromatography on silica-gel eluting with chloroform–methanol (98:2). Two bands were obtained: R_f 0.32, identified as **5**: R_f 0.24, identified as a mixture of **6** and **4** and yielding **4** after crystallisation from ethanol.

10-Fluorotetrazolo[1,5-f][1,5]phenanthroline **5** crystallised from ethanol as needles, m.p. 218–220 °C. HRMS: Calc. $C_{12}H_6FN_5$ 239.0607. Found: 239.0606. ^1H NMR: δ 7.64 (11-H, $J_{9,11}$ 2.5, $J_{H,F}$ 8.5), 7.81 (6-H, $J_{5,6}$ 8.5, $J_{6,7}$ 4.5), 8.77 (9-H and 12-H, m), 8.95 (5-H, $J_{5,6}$ 8.5, $J_{5,7}$ 1.5), 9.05 (7-H, $J_{6,7}$ 4.5, $J_{5,7}$ 1.5). MS EI: *m/z* (%) 239 (23, M^+), 211 (100, $M^+ - N_2$).

10-Fluorotetrazolo[1,5-f][3,5]phenanthroline **4** crystallised from ethanol as needles, m.p. 264–266 °C. HRMS: Calc. $C_{12}H_6FN_5$ 239.0607. Found: 239.0598. ^1H NMR: δ 7.69 (11-H, $J_{9,11}$ 2.5, J_{HF} 8.7), 8.21 (9-H, $J_{9,11}$ 2.5, J_{HF} 9.5), 8.26 (8-H, $J_{7,8}$ 6.0), 8.88 (12-H, $J_{11,12}$ 8.7, J_{HF} 4.5), 9.06 (7-H, $J_{7,8}$ 6.0), 10.06 (5-H, s). MS EI: *m/z* (%) 239 (19, M^+), 211 (100, $M^+ - N_2$).

Reaction of 5-(2-chloro-4-fluorophenyl)-1-(quinolin-3-yl)-tetrazole. The title compound (50 mg) in electrolyte (15 cm^3) was reduced at a cathode potential of −1.75 V vs. SCE. After 8 min the current fell to a low value with the passage of 1.29 F mol^{-1}. The reaction mixture was evaporated to dryness under reduced pressure, after which the residue was dissolved in dichloromethane washed with water and dried, and the relative yields of **9**, **10** and **11** determined (Table 1). The dihydro compound **11** was identified by dehydrogenation of the mixture using 2,3-dichlorodicyano-1,4-benzoquinone in refluxing benzene to follow the conversion of **11** into **10** by ^{19}F NMR spectroscopy. The products of the electrochemical reaction were separated by thin layer chromatography on silica gel using multiple elution with dichloromethane.

12-Fluorodibenzo[c,f]tetrazolo[1,5-a][1,7]naphthyridine **10** crystallised from ethanol as needles, m.p. 266–269 °C. HRMS: Calc. $C_{16}H_8FN_5$ 289.0764. Found: 289.0765. ^1H NMR: δ 7.75 (13-H, $J_{13,14}=J_{H,F}$ 7.7, $J_{11,13}$ 2.5), 7.95 (8-H and 9-H, multiplet), 8.45 (10-H, $J_{9,10}$ 8.5, $J_{8,10}$ 2.0), 8.83 (11-H, $J_{H,F}$ 11, $J_{11,13}$ 2.5), 8.97 (7-H, $J_{7,8}$ 8, $J_{7,9}$ 2.0), 9.02 (14-H, $J_{13,14}$ 8.7, J_{HF} 6), 10.28 (5-H, singlet). MS EI: *m/z* (%) 289 (7, M^+), 261 (100, $M^+ - N_2$).

12-Fluorobenzo[b]tetrazolo[1,5-f][1,5]phenanthroline **9** crystallised from ethanol as needles, m.p. >290 °C. HRMS: Calc. $C_{16}H_8FN_5$ 289.0764. Found 289.0757. ^1H NMR: δ 7.64 (13-H, $J_{HF}=J_{13,14}$ 8.5, $J_{11,13}$ 2.5), 7.80 (7-H, $J_{7,8}=J_{6,7}$ 7.5), 7.97 (8-H, $J_{7,8}=J_{8,9}$ 7.5), 8.17 (6-H, $J_{6,7}$ 7.5), 8.40 (9-H, $J_{8,9}$ 7.5), 8.77 (14-H, $J_{13,14}$ 8.5, J_{HF} 5), 8.98 (11-H, J_{HF} 9.8, $J_{11,13}$ 2.5), 9.39 (5-H, singlet), NOE enhancement of 6-H by 7% was observed upon irradiation of 5-H. MS EI: *m/z* (%) 289 (9, M^+), 261 (100, $M^+ - N_2$).

Reaction of 5-(2-fluoro-6-iodophenyl)-1-(quinolin-3-yl)-tetrazole. The title compound (50 mg) in electrolyte (15 cm^3) was reduced at a cathode potential of −1.50 V vs. SCE. After 6 min the current fell to a low value with the passage of 1.38 F mol^{-1}. Work-up afforded a mixture of **12**, **13** and **2d** (see Table 1). Pure samples of **12** and **13** were separated from the photochemical reaction of the title compound and identified by their ^1H NMR spectra. The third product **2d** was identified by comparison with a sample described earlier in this paper.

Photochemical reactions. A solution of the tetrazole (200 mg) in acetonitrile (150 cm^3) was irradiated 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 to dryness under reduced pressure and the components analysed by ^{19}F NMR spectroscopy.

5-(2-Chloro-4-fluorophenyl)-1-(pyridin-3-yl) tetrazole was irradiated for 15 h during which time the reaction had reached 90% completion. Two products **4** and **5** were detected (Table 1).

5-(2-Chloro-4-fluorophenyl)-1-(quinolin-3-yl) tetrazole was irradiated for 72 h after which time ^{19}F NMR spectroscopy showed only the presence of unreacted starting material.

5-(2-Fluoro-6-iodophenyl)-1-(quinolin-3-yl) tetrazole was irradiated for 2 h during which time the reaction had reached 90% completion. Two products **12** and **13** were detected (Table 1). These were separated by thin layer chromatography on silica gel eluting with chloroform–methanol (98:2).

14-Fluorodibenzo[c,f]tetrazolo[1,5-a][1,7]naphthyridine **13** R_f 0.30 crystallised from ethanol as needles, m.p. 269–272 °C. HRMS: Calc. $C_{16}H_8FN_5$ 289.0764. Found: 289.0759. ^1H NMR: δ 7.77 (13-H, $J_{12,13}=J_{HF}$ 8.5), 7.90 (8-H, $J_{7,8}=J_{8,9}$ 7.5, $J_{8,10}$ 2), 7.96 (9-H, $J_{8,9}=J_{9,10}$ 7.5, $J_{7,9}$ 2), 8.05 (12-H, multiplet), 8.45 (10-H, $J_{9,10}$ 7.5), 8.97 (7-H and 11-H, multiplet), 10.35 (5-H, singlet). MS EI: *m/z* (%) 289 (7, M^+), 261 (100, M^+-N_2).

14-Fluorobenzo[b]tetrazolo[1,5-f][1,5]phenanthroline **12** R_f 0.40, crystallised from ethanol, m.p. >290 °C. HRMS: Calc. $C_{16}H_8FN_5$ 289.0764. Found: 289.0750. ^1H NMR: δ 7.69 (13-H, $J_{12,13}=J_{HF}$ 9), 7.80 (7-H, $J_{6,7}=J_{7,8}$ 8.5), 7.98 (8-H and 12-H, multiplet), 8.18 (6-H, $J_{6,7}$ 8.5), 8.40 (9-H, $J_{8,9}$ 8.5), 9.20 (11-H, $J_{11,12}$ 7.5), 9.42 (5-H, singlet), NOE enhancement of 6-H by 7% was observed upon irradiation of 5-H. MS EI: *m/z* (%) 289 (14, M^+), 261 (100, M^+-N_2).

Reactions with tributyltin hydride. A solution of the tetrazole (0.27 mM) in dry benzene (10 cm^3) was refluxed under nitrogen with tributyltin hydride (0.72 cm^3, tenfold excess) and azoisobutyronitrile (5 mg). For bromo and iodo compounds reaction was complete after 48 h and 24 h, respectively. For chloro compounds the reaction mixture was worked up after 72 h although **14**, X=Cl showed only 9% conversion, while **2a** and **2b** did not react. After reaction, the solvent was removed under reduced pressure. The residue was dissolved in acetonitrile (20 cm^3) and extracted with dry hexane (4 × 20 cm^3). Two layers formed and the tributyltin compounds dissolved in the hexane layer. The acetonitrile layer, free of tin compounds, was collected and the solvent removed to leave a mixture of products and unreacted starting material. The amount of unreacted starting material and the yields of products were determined by ^{19}F NMR spectroscopy. Yields for the reactions of **14**, X=Cl, Br or I, are given in Table 2. Compound **2c** gave 48% of **2d**, 30% of **11** and 22% of **10**.

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